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THE PREPARATION OF CELLS FOR THE MEASUREMENT OF HIGH OSMOTIC PRESSURES.

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In an article describing "The Preparation of Osmotic Membranes by Electrolysis,"[1] the following opinion was expressed: "It seems improbable that the total osmotic pressure of concentrated solutions, *e. g.*, molecular normal ones, will ever be directly measured." The results of further work in this field have led to a revision of that judgment. It has been found that a much more satisfactory membrane can be made by electrolysis than was anticipated when the first communication on the subject was written. At that time pressures of 4.5 atmospheres had been reached. The inability to attain to higher pressures was due, as was then explained, not to the weakness of the membranes, but to the impossibility, with the means employed up to that time, of securing the manometer in the cell. With improved arrangements for securing the manometer, and with such alterations of cell con-

[1] This JOURNAL, 26, 80.

struction as our later experience has shown us to be necessary, we have attained to a pressure of about 31.5 atmospheres with a normal solution of sugar. During the past year our efforts have been directed almost exclusively to the construction of satisfactory cells, and not to the careful measurement of osmotic pressures, the former problem being obviously the really serious obstacle in the way of the direct measurement of this force.

The problem has not yet been solved to our entire satisfaction, but considerable progress has been made, and we propose to describe some of the difficulties which we have experienced in the course of our work and the means which we have employed to overcome them.

Porous cups, such as are used for other purposes, were found unsuitable for the construction of osmotic cells in which high pressures were to be developed, and we were compelled to enlist the aid of the potters in order to obtain cups which should meet our requirements. The ordinary porous cup is too soft, and, therefore, too weak, and is usually made of too coarse material. Its walls are also likely to contain cavities of such size as to interfere with the best results in membrane formation. Our experience has shown us that the best effects are produced in cups made of rather fine materials, very uniformly mixed, and hard burned. A high degree of porosity is not essential, while the hard burning of the cups greatly increases their strength. That great strength is necessary will be understood when we state that the total pressure attained in some of our cells amounted to over 3,000 kilograms. The bursting of the cups before the maximum pressure was reached has not been an unusual occurrence.

We have had made for us, in accordance with specifications which seemed likely to yield a satisfactory product, two varieties of cups which differed principally in respect to the internal dimensions and to the thickness of the walls. One of these has a depth of 75 mm., an internal diameter at the top of about 22 mm., and at the bottom of 18 mm. The thickness of the wall is about 4 mm. At the top of the cup there is a rim with a thickness equal to that of the wall and a depth of

8 mm. The other variety of cup has a depth of 80 mm., an internal diameter at the top of 25 mm., a wall twice as thick as the first, and a thicker and wider rim.

One of the cups of the thinner-walled variety remained unbroken at a pressure exceeding 30 atmospheres, while others have cracked under a pressure as low as 17 atmospheres. Our experiments thus far have been mainly with the thinner cups, and we are unable to state what pressures the thicker ones may be expected to stand.

The accompanying figure (Fig. I.) represents the earlier form of our apparatus. It consists of the porous cup *A*, the glass tube *B*, and the closed manometer *C*. The lower end of the glass tube is provided with a narrow rubber ring, *a*, of such thickness as to fill very tightly the space between the glass and the wall of the cup. In order to give the cement (litharge and glycerine) which is used to fill the space above the rubber ring a more secure hold upon the wall, one or more channels are cut in the wall by slowly turning the cup around a rapidly revolving carborundum or emery disk. The upper exposed surface of the cement is painted with a solution of rubber, or of rubber and paraffin, in carbon bisulphide. The upper end of the glass tube is considerably contracted by softening the glass in the flame, the purpose being to give the rubber stopper carrying the manometer greater security in its place, and to crowd the rubber toward the manometer tube and thus diminish the danger of leakage between it and the latter. A short distance below the upper end of the tube the

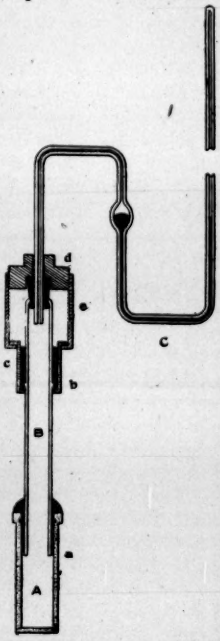


Fig. I.

ring *b* is made. The brass piece *c* is fastened in its place with the usual litharge-glycerine cement. The nut *d*, through which the manometer passes before entering the rubber stopper, is threaded to fit the collar *e*. By turning *e* while the nut is held, the stopper may be crowded into the tube and any desired initial pressure produced within the cell. The manometer tube has a base of about 1 mm. The length of the graduated portion is from 30 to 70 cm., which is carefully calibrated by means of mercury threads before closing the tube at the top. The volume of the calibrated space is also determined by weighing the mercury which fills it. To prepare the manometer for use, it is attached by means of a rubber tube to another glass tube of the same kind as the manometer itself, and filled with mercury. Air, which has been freed from carbon dioxide by means of potassium hydroxide, and which has been dried over resublimed phosphorus pentoxide, is then drawn into the manometer after the receding mercury until the calibrated portion of the tube has been filled at atmospheric pressure. The manometer is then closed by fusing the glass at the upper end. In order to avoid a possible contamination of the air in the manometer with carbon dioxide, the central portion of a large platinum disk is heated by the blowpipe to a high temperature, and having slightly diminished the pressure on the gas within, the end of the manometer, as soon as it is detached from the supply of dried air, is passed quickly over the heated spot on the side of the disk opposite to the blowpipe. In this way the tube is almost instantly closed, and the only possible contamination of the air is a trace of water vapor. The pressure within the manometer is then still further reduced and the glass at the end thickened by softening it in a small flame.

The closing of the manometer in this way introduces, of course, some uncertainty as to the exact volume of the upper end, which sometimes has a spherical and sometimes a conical shape, and it will be necessary, when exact measurements of osmotic pressure are attempted, to cut off and recalibrate the upper end of the manometer after the work of measuring has been completed. This will be especially necessary when high

pressures are to be measured—when, for example, as in some of the cases which we shall mention hereafter, a rise of 1 mm. in the mercury amounts to nearly a whole atmosphere of pressure. For purposes of exact measurement, however, it will probably be advisable to use much longer manometers. Having filled the manometer, the air in it is brought to atmospheric pressure by raising or lowering the attached tube, its volume and temperature are ascertained, and its volume under standard conditions calculated.

The method which was employed earlier to remove the air from the walls of the porous cup has been found to work very satisfactorily. As formerly, the cell, when finished, is filled with a 0.05 per cent solution of potassium sulphate and surrounded by the same liquid. A current is passed from an electrode outside of the cell to one within, the voltage being raised until an "endosmose" in the inward direction is obtained which amounts to about 500 cc. per hour. After about a liter of liquid has been forced through the walls in this manner, the solution of sulphate is replaced by distilled water and the current again passed for some time. This procedure is repeated until the liquid almost ceases to conduct the current. The cell is then immersed and allowed to stand in recently boiled distilled water until required for the formation of the membrane. To prepare the latter, the emptied cell is placed in a beaker glass. A long platinum rod, which is to serve as cathode, is lowered into the cell. As anode, a cylinder of copper is used. There is also inserted in the cell a siphon, which reaches very nearly to the bottom of the cup and is closed at the outer end with a piece of rubber tubing and a pinch-cock. The purpose of the siphon is to remove the liquid from the cell from time to time in order to prevent an accumulation of alkali, which is believed to affect the membrane injuriously if present in more than minute quantities. When all is in readiness and the circuit closed, the potassium ferrocyanide (N/10) and the copper sulphate solution (N/5) are introduced simultaneously, the former into the cell and the latter into the beaker containing the anode and the cell. In the beginning, owing to the fact that the porous walls are

filled with nearly pure water, there is very little current. The current, however, within a minute or two begins to increase. Then, within a very short interval, it begins to fall, and continues thereafter to decrease steadily until the maximum resistance of the cell is reached. This varies greatly. Ordinarily it is above 10,000 ohms, often double this amount, and in one case it exceeded 200,000 ohms. We are not yet satisfied that this variation in the maximum resistance of the different cells is dependent exclusively upon the membranes themselves. We have had reason, on some occasions, to suspect that a failure to reach very high resistances was due to defects in the construction of the cell or to the character of the porous wall, and not to the resisting power of the membrane. The formation of a membrane, that is, the time required to reach the highest resistance, usually occupies from one to two hours. We cannot yet give any definite opinion as to the electromotive force which it is most advantageous to employ. We use in our work a one horse-power motor-generator, which transforms a 110-volt battery current to 250 volts. We have in series with the field of the dynamos a rheostat of so wide a range that we are able to depress the voltage by small intervals from its maximum, *i. e.*, 250 to 30 volts. We are under the impression, however, that the lower voltages are not advantageous and have ordinarily employed an electromotive force ranging from 110 to 150 volts. We are, furthermore, under the impression that when a perfect cell has been constructed an even higher voltage will be found to be desirable. We have, of course, made a great many observations in connection with the amount of electromotive force employed in forming the membranes, but they have little value because the principal difficulties which we have had to meet have not had their cause in defects of the membrane, but were due rather to other features in the construction of the cell. In other words, we have not been able to connect, in cases of failure to obtain satisfactory results, the cause of the failure with the voltage which had been employed in making the membrane. During the formation of the membrane it has been our practice to withdraw the solution of ferrocyanide

from the cell and to replace it with a fresh one once every three or four minutes, somewhat oftener during the earlier than in the later stages. If the alkali is allowed to accumulate in the cell, the membrane, or parts of it, sometimes acquires a dark-brown color, apparently due to the formation of copper oxide. It was stated in the earlier communication that the membrane is located within the wall about equidistant from the two sides. This has been found to be true only of comparatively soft cups. In the hard-burned ones, which we are now using, the membrane is always deposited upon the interior surface of the cup and extends into the wall only where there are minute cavities, and in these it is continuous from the interior surface to the end of the cavity, so that one often sees, after breaking a cup, brown streaks on the fracture-surfaces, extending in some cases half way through the wall. Having completed the formation of the membrane, the cell is emptied, several times rinsed within and without with distilled water, and then, if not immediately required, it is placed in distilled water, filled with the same, and allowed to stand until needed for use.

We have used thus far, for the purpose of testing our cells, only half-normal and normal solutions of sugar. To these we have added a small quantity of potassium ferrocyanide, usually just enough to make the solution N/100 or N/1000 with respect to the salt. To the distilled water, with which the cells were surrounded, there has been added a chemically equivalent quantity of copper sulphate. That is, if the sugar solution within the cell was N/100 with respect to potassium ferrocyanide, the water without was made N/100 with respect to copper sulphate. And if the sugar solution was N/1000 with respect to the first salt, the water without was made N/1000 with respect to the second. Such solutions are, of course, not exactly equivalent osmotically, there being a slight advantage in favor of the sugar solution, owing to the fact that the potassium ferrocyanide molecule dissociates into five ions, while 2 molecules of copper sulphate yield only four, and also to the fact that the former salt is somewhat more highly dissociated than the latter. The use of the ferrocyanide and of the sul-

phate in this way is of assistance in the detection of breaks and other leaks in the cell.

The capacity of the cells made with the thinner cups has varied from 50 to 70 cc., according to the diameter and length of the glass tube. Before filling, they are rinsed a number of times with small quantities of the sugar solution which is to be used. To provide for the overflow which must occur when the stopper is inserted, we have employed a little implement made from an ordinary round file. On one side of the untempered end of the file a channel is cut. The end is then bent to a hook shape, filed down and smoothed to avoid scratching the glass. This is inserted with the stopper and allowed to remain until the latter has been crowded into the glass tube as far as it can be made to go by the hands. It is then withdrawn, the brass nut is lowered upon the stopper, and the metal collar screwed up until the nut begins to exert a slight additional pressure upon the stopper, which is indicated by the rise of the mercury in the manometer. At this point the cell is placed in water and fixed in its position. The nut is then held by means of a wrench, while the collar is turned in order to drive the stopper somewhat further into the glass tube. Ordinarily, we have forced the stopper down in this manner until the manometer indicated a pressure of from one to two atmospheres.

After closing the cell and screwing up the brass collar, the mercury in the manometer usually begins to rise within a few minutes and continues to do so until the maximum pressure is reached or until some defect in the cell is developed. The rise is frequently very rapid at first, corresponding in some cases of normal solutions to an increase of pressure of 10 or more atmospheres (and in one instance over 20 atmospheres) within an hour. At other times the rise of the mercury is slow, but in such instances the cells usually develop defects at comparatively low pressures, and apparently the slow increase of the pressure is due not so much to the difference in the activity of the membranes of individual cells as to the fact that the defects operate from the beginning, but not for some time in a sufficient degree to counterbalance the increase of pressure.

We have not made any systematic observations on the rate at which pressures develop, because data of this kind are of little value as long as the evolution of the cell is incomplete, that is, until a cell has been produced which will surely stand, without failures of any kind, the maximum pressures of the solutions for which it is intended. It can, however, be said in general, as would be expected, that the rate at which the pressure in the cell increases constantly diminishes.

It has been predicted that a serious obstacle in the way of the direct measurement of osmotic pressure would be found in the long time which would probably be required for the development of the maximum pressures of solutions. But we have discovered no reason so far for thinking that this fear will be realized. We are not able to affirm that we have obtained the maximum pressures of either normal or half-normal solutions, but we have probably very nearly reached the limits for both of these concentrations, and the time occupied in doing so has not, in any case, been very long.

The cell in its original form developed a number of serious defects:

1. The glass tube, on one occasion when the pressure in the cell exceeded 26 atmospheres, was pushed upward through the cement with which it was fastened in the cup. This difficulty was easily remedied by slightly enlarging the tube just above the rubber band.

2. The glass tube, notwithstanding careful annealing, frequently broke at or near the ring at the upper end. This difficulty was remedied in the same manner as the first by replacing the ring with a small bulb blown in the tube.

3. The liquid was often forced out of the cell between the rubber stopper and the manometer tube. This has been one of the most persistent of our troubles and it has not yet been fully mastered. We have greatly diminished, and sometimes entirely removed, the difficulty by placing between the stopper and the nut, through which the manometer passes, a brass ring which had been hollowed out to a conical form upon the under side, and by tightly winding the upper end of the stopper with narrow strips of insulating tape. The effect of

this arrangement is to crowd the upper end of the stopper more and more tightly against the manometer as the stopper is forced downward by the nut above. Another device designed to produce the same effect will be described later. On four occasions the manometer itself has been pushed upward out of the rubber stopper. The cause of this is, of course, the same, namely, the failure to crowd the rubber sufficiently hard against the manometer tube.

4. It was found, in several instances, that the cement employed to fasten the glass tube into the cup had been somewhat disintegrated by the action of the liquids which penetrated the wall of the cup from the outside and came into contact with it. And the failure of a number of our cells to develop more than very moderate pressures is to be ascribed to this cause. The measures adopted to overcome this difficulty will be better explained when we come to describe the most recent form of our cell. It is sufficient to say here that we now line the cavity occupied by the cement with a coating of rubber, which is afterwards hardened or vulcanized. By this process, together with the painting of the upper exposed surfaces of the cement with rubber, we prevent any contact whatever of the cement with liquids.

5. We have stated that the rubber band at the bottom of the glass tube was crowded very tightly against the wall of the cup, and especial pains has been taken to give the lower edge of the rubber as much support as possible in this way. Nevertheless, our cells have failed more frequently in consequence of a slight movement under pressure of the lower edge of this band than from any other one cause. The upper limit of the membrane is at the lower edge of the rubber band, and if the rubber is pushed upward or sidewise in the slightest degree, as it often has been, a portion of the wall not covered by the membrane is exposed and a leakage into the wall is the result. It was mainly for the purpose of detecting a leak of this kind that we have been accustomed to add a little potassium ferrocyanide to the sugar solution and a little copper sulphate to the water in which the cell was immersed. It should also be said that at times there has been a leakage of

the sugar solution between the rubber band and the glass tube into the cement. The failure of the rubber band to remain rigid can be detected when the leakage is into the wall of the cup by the peculiar movements of the mercury column in the manometer. The mercury rises continuously, and perhaps rapidly, until a pressure of several atmospheres is indicated, then suddenly it falls perhaps 2 or 3 mm., then begins to rise again, going the second time higher than before, at times very considerably higher. It then falls again as before, only to be succeeded by another and higher rise of the mercury. This conduct is clearly due to the formation of new membranes over the surface exposed in consequence of the crowding up or aside of the lower edge of the rubber band. When a leakage at the stopper occurs, the movements of the mercury column are usually somewhat different from those just described. The first effect of the leakage is ordinarily a marked diminution in the rate at which the mercury rises. This slackening becomes more and more pronounced until at a certain point the column suddenly falls a few millimeters. It then rises about to the point it first reached and falls again as before. Usually this behavior continues until the cell is taken apart. In such cases it is evident that the liquid is forced out from time to time in small portions and only as a certain definite pressure is reached. The process may continue until the contents of the cell have become considerably diluted, but as the dilution proceeds the time required for the mercury, after a fall, to reach its previous elevation naturally increases. Sometimes, however, when a leak at the stopper occurs, the mercury rises rapidly at first, then much more slowly, but continuously, until its highest point is reached, where it remains perhaps for days, if the leak is a minute one, without sensible movement in either direction. The meaning of this conduct is, of course, that the leak is continuous and not intermittent as in the first case. Frequently, when a cell gave indications of a movement of the rubber band, we have taken it apart, washed it, and then subjected it to the same treatment as when the membrane was first formed, that is, we have attempted to deposit electrolytically

a membrane over the places exposed in consequence of the movement of the rubber band. Occasionally this treatment has been repeated as many as three times with the same cell, and usually the process has been satisfactory to this extent, that we were able, after such a course, to obtain considerably higher pressures than at first. But not any of the cells which proved themselves defective in respect to the rubber band have ever given us what we suppose to be the maximum pressures of the solution.

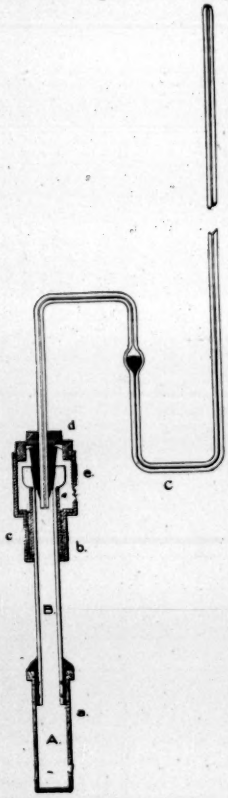


Fig. II.

In the new form of cell (Fig. II.), we have substituted a porcelain tube for the glass one. We were led to do so by certain unpleasant experiences with the material from which our glass tubes were made. All the cells made during a period of several weeks were lost in consequence of the cracking of the glass tubes, often in the most unexpected places and apparently without cause. The real explanation is probably that the glass, which had been in the laboratory for some years, had suffered deterioration. Another reason for making use of porcelain instead of glass was that the portion occupied by the rubber stopper could be ground into a form which seemed likely to diminish the difficulty which we have always had in keeping the stopper and the manometer in their places. The porcelain tubes which were available for our purposes were un-

glazed ones and we feared, notwithstanding the fact that they had evidently been heated to very high temperatures, that they would develop leaks under high pressures. To test them with respect to their possible porosity, we plugged one end and soaked them over night in a salt solution, and then tested the walls as to their conductivity between the poles of our dynamo while developing 250 volts. No current could be detected. In order to make use of the porcelain tubes according to our new plan for the cell, it was necessary to grind a portion of one end—the one located in the cup—perfectly round externally, and at the other end to grind a "seat" for the rubber stopper, which should have a taper somewhat greater than the stopper itself. The proper centering of the tube for grinding of this kind cannot be accomplished by any of the usual tools of the mechanic. We therefore made for ourselves the "chuck" which is represented in Fig. III. *A* is a steel tube having a length of 12.5 cm., and a hole 2.5 cm. in diameter from end to end. Near each end are three machine screws symmetrically located around the tube. The porcelain tube, which is to be shaped, is fastened between the ends of the two sets of three screws each. This arrangement permits any desired adjustment of either end of the tube. Around the central portion of the steel tube *A* is an accurately fitted steel ring, *B*, which is provided with oil holes. At each end of the ring there is a collar, *C*, with a set screw. As all parts of the tool are perfectly fitted, the tube *A* turns in its collar easily and accurately. The ring itself is made stationary between

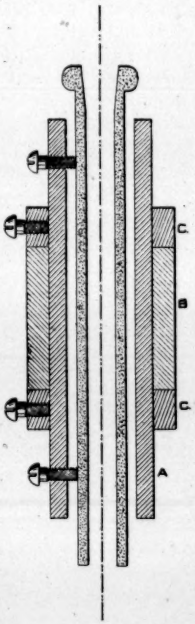


Fig. III.

the jaws of the "back-rest" of the lathe. The porcelain tube, after adjustment, may be turned during the grinding by the hand, or by a pulley and belt, or the tube may be joined to the "live" spindle of the lathe. The grinding is done by means of carborundum or emery disks fastened upon the ends of small steel mandrels which are held in the chuck of a "traveling" grinder, the grinder being attached to the tool-carriage of the lathe. This being compound, the grinding disk may be made to move back and forth at any angle to the axis of the porcelain tube. The grinder which we use has a speed which may be varied between 2,000 and 5,000 revolutions per minute. At these rates the porcelain can be quickly shaped without danger of impairing the strength of the tube, since the grinding disk may be made to touch the porcelain so lightly that there is practically no jarring of the tube.

As stated already, the seat for the stopper is given a somewhat greater taper than that of the stopper itself. The result of this form is that, as the stopper is pressed forward into the tube, it is crowded more and more tightly against the manometer tube. Another device which has been of great assistance to us in securing the manometer in the rubber stopper may be mentioned here. The end of the manometer tube is made to project 2.5 or 3 cm. beyond the lower end of the stopper and is heated to a temperature somewhat above the fusing-point of shellac, and while hot, covered with the gum in order to secure good adherence to the glass. Afterwards portions of molten shellac are deposited upon the tube near the stopper and allowed to solidify until a considerable quantity has accumulated. The tube is then held vertically and the shellac cautiously and uniformly heated, but not so high as to produce a thin fluid condition. In this state it gradually descends and solidifies, forming upon the tube a conical enlargement. Now if the tube is forced upwards under the pressure in the cell, the apex of the cone enters the stopper, spreading the rubber sidewise, tightening both stopper and manometer in their places.

In order to give the cement a more secure hold upon the

porcelain tube, there are cut into the tube in that portion covered by the former, a number of horizontal gashes or furrows, a grinding-disk with a wedge-shaped edge being employed for the purpose.

The arrangement for securing the stopper is necessarily somewhat more complicated than when a glass tube is used. A short brass tube, somewhat smaller than the enlarged upper end of the porcelain one, is placed over the latter, and with its edge lying against the shoulder, is filled with cement. The lower edge of this brass tube serves the same purpose as the bulb at the upper end of the glass tube in the earlier form of the cell, that is, it rests upon the flange of the brass piece on which the threaded collar turns.

The substitution of a rigid ring of hard rubber or of soapstone for the rubber band, which was first used at the bottom of the tube, and which has given us so much trouble, made it necessary to grind the inner wall of the cup quite accurately as far as the lower edge of the ring. This gives us a shoulder in the cup on which the ring rests.

In order to center the cup in the lathe for the purpose of grinding the inner wall, we have employed the chuck represented in Fig. IV. It consists of the master-chuck *A*, which is screwed on to the mandrel of the lathe and the brass tube *B*, which is screwed into the master-chuck. The inside of *B* is threaded from end to end, and in it there are the two smaller threaded tubes *C* and *C'*. At one end of *C* and *C'* there is a flange, against which rest the soapstone rings *D* and *D'*. These rings are bored to a taper equal to that of the outside of the cups. The largest diameter of the hole in the forward ring is slightly less than that of the cup under the rim, while the largest diameter of the rear one is equal to that of the cup about one-third of the way from the bottom. With this arrangement it is practicable to center the cup quite satisfactorily and to hold it sufficiently firmly in its place during the process of grinding. The grinding is accomplished by means of carborundum disks held in the chuck of the traveling grinder already referred to.

The rings are turned to fit the ground end of the porcelain

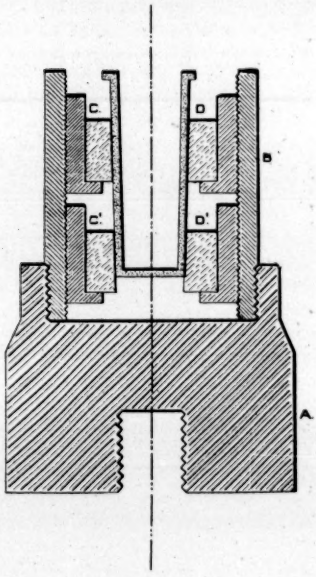


Fig. IV.

tube and the inner wall of the cup with the greatest possible exactness.

After grinding the porcelain tube and the cup and turning the ring, the ring is fixed in its position upon the ground end of the porcelain tube and firmly against the shoulder above. The tube is then inverted and the ring soldered to it with shellac, the shellac being maintained in the molten condition for some time in order that it may work its way inward between the two. The lower end is then painted two or three times with a solution of rubber in carbon bisulphide, and the rubber is afterwards hardened by maintaining it for several hours at a temperature of from 90° to 100°.

The ring with the tube firmly attached in the manner described is placed in position on the shoulder within the cup. The cup wall above the ring is then repeatedly painted with the rubber solution. A quantity of shellac is placed upon the ring and the temperature of the cup raised until the gum fuses. It is kept in the molten condition for some time to insure its working its way between the outer edge of the ring and the wall of the cup. The cup is then placed in a hot air-bath and kept at a temperature of from 90° to 100° for several hours, or until the rubber on the wall is no longer sticky. Finally the space above the ring is filled with the cement. It is to be noted with regard to the latter that the hardening process is much more rapid if a little water is added to the glycerine with which the litharge is mixed.

Our observations on the osmotic pressures of half-normal and normal solutions of sugar have thus far been made with reference to the testing of the construction of our cells and the efficiency of the membranes prepared by the electrolytic process, and not with a view to an accurate determination of the pressures of such solutions. Nevertheless, we have accumulated some data which enable one to predict approximately what the pressure of a half-normal solution will be found to be, and to state that the pressure of a normal solution will be found to be above a certain definite value. We give below a brief record of the greater portion of the cells which were made after we had remedied the difficulties which resulted from the use of a flexible rubber ring at the bottom of the glass tube, and those which were occasioned by permitting the solutions, during the electrolysis, to soak through the cup wall where they could come in contact with the cement. It should be stated, with reference to these records, that the atmospheric pressure, *i. e.*, that upon the water outside of the cell, is, in every case, deducted from the pressure upon the air within the manometer; also that the volumes of the air within the manometer are reduced to 0° for all observations, so that the pressures recorded are simply osmotic pressures at the temperatures of the cells when the readings were made. These readings were obtained with the aid of a

standard meter and a cathetometer of the best construction, the telescope of which is provided with a micrometer eye-piece, supposed to enable one to read with a fair degree of accuracy to within $\frac{1}{100}$ mm. The values given are to some extent inaccurate in consequence of the uncertainty as to the exact form of the upper end of the manometer. As previously stated, when the manometer was closed by fusing the glass, the form of the upper end of the air space was sometimes spherical and sometimes conical in appearance, and we have assumed in our calculations that it was either perfectly spherical or conical according to the form which it resembled more closely. The error resulting from this uncertainty does not, however, exceed in any case 0.2 atmosphere and in most cases is much less than this. When we undertake to determine with accuracy the pressures of solutions, we shall, of course, after having made our measurements, open the manometers and recalibrate the upper ends.

Observations on the Osmotic Pressure of Half-Normal Solutions.

1. Resistance of the membrane, 16,307 ohms. The pressure rose in twenty-five hours to 11.34 atmospheres at 23°.1, when the manometer was pushed out of the cell.

2. Same cell as No. 1. Resistance of the membrane, 16,307 ohms. The pressure rose in twenty-two and a half hours to 13.2 atmospheres at 24°.3, when the manometer was accidentally broken.

3. Resistance of the membrane, 108,000 ohms. Filled with a sugar solution which had been made ten days before. The pressure rose in twenty-five hours and fifteen minutes to 14.51 atmospheres at 22°.8. Cell taken down and solution examined with Fehling's solution. The sugar was found to be somewhat inverted.

4. Resistance of the membrane 110,000 ohms. Filled with a fresh solution of sugar which did not reduce Fehling's reagent. The pressure rose slowly in ninety-five hours and twenty-six minutes to 12.78 atmospheres at 25°.6. The cell is believed to have leaked at some point, but the defect could

not be located with certainty. The solution, after removal from the cell, reduced Fehling's solution very slightly.

5. Resistance of the membrane, 12,111 ohms. Filled with a fresh solution of sugar. The pressure rose to 11.83 atmospheres in forty-seven hours. The cell was found to be leaking and was taken down.

6. Resistance of the membrane, 14,625 ohms. Solution of sugar not freshly made. The pressure rose to 13.52 atmospheres at 23°.4 in fifty-two hours and forty minutes, when the manometer was forced out of the cell.

7. Resistance of the membrane, 29,000 ohms. Filled with a fresh solution of sugar. The pressure rose in two hours and fifty minutes to 8.94 atmospheres; in the following three hours and fifty minutes to 12.33 atmospheres; in the succeeding four hours and forty minutes to 13.39 atmospheres; and then in the next eighteen hours, to 13.58 atmospheres at 20°.5. The pressure remained constant for thirty hours longer, when the cell was taken down. The solution was not examined for inversion.

8. Resistance of the membrane, 110,000 ohms. Filled with a fresh solution of sugar. The pressure rose in one hour and forty minutes to 7.72 atmospheres; in the following seventeen hours and thirty minutes, to 10.56 atmospheres; in the succeeding ten hours and forty-five minutes, to 13.10 atmospheres; then in thirty-three hours and forty-five minutes, to 14.03 atmospheres. The pressure then remained practically constant for seventy-two hours, the last reading being 14.08 atmospheres at 25°.2 when the cell was taken down. The solution from the cell was accidentally lost, and therefore not examined for the inversion which our experience with other cells leads us to believe had occurred to some extent.

Observations on the Osmotic Pressure of Normal Solutions.

1. Resistance of the membrane, 3,303 ohms. The pressure rose in fifteen hours to 16.62 atmospheres, when the porous cup burst.

2. Resistance of the membrane, 6,316 ohms. The pressure rose in forty-one hours to 16.61 atmospheres, when the cell was found to be leaking at the stopper.

3. Same cell as in No. 2, but resubjected to the membrane-forming process. Resistance, 2,698 ohms. The pressure rose in sixty-nine hours to 22.02 atmospheres at 22°.3. The manometer was displaced by the pressure and the cell was found to be leaking at the stopper.

4. Resistance of the membrane, 16,000 ohms. The pressure rose to 19.6 atmospheres in six hours, when the manometer was pushed out of the stopper.

5. Resistance of the membrane, 21,000 ohms. The pressure rose in three hours and twenty-five minutes to 19.32 atmospheres, and in the succeeding twelve hours to 22.88 atmospheres. The cell was then found to be leaking. It was opened, but as there appeared to be no escape of liquid around the stopper it was closed again without change of contents. In ten hours the pressure rose to 22.01 atmospheres, when it began to fall and the cell was taken down.

6. Resistance of the membrane, 7,648 ohms. The pressure rose in seven hours and 42 minutes to 21.98 atmospheres, when the porous cup burst.

7. Resistance of the membrane, 6,750 ohms. The pressure rose in five hours and forty-five minutes to 19.3 atmospheres. Cell found to be leaking at the stopper. It was refilled, and in four hours and thirty minutes the pressure rose to 18.68 atmospheres. As the pressure would rise no higher the cell was taken down for investigation.

8. Resistance of the membrane, 6,000 ohms. The pressure rose in seventeen hours and forty-five minutes to 21.42 atmospheres. The cell was found to be leaking around the manometer tube. It was refilled, and in five hours and thirty minutes the pressure rose to 26.96 atmospheres at 21°. During the five succeeding days there was no noticeable change of pressure, but at the close of this period the cement gave way and the glass tube was pushed out of the cell. The sugar solution used in this experiment was freshly made and free from invert sugar. It was made only N/1000 with respect to potassium ferrocyanide.

9. Resistance of the membrane, 12,033 ohms. Solution N/100 with respect to potassium ferrocyanide. The following are the data concerning the pressures developed :

Pressure at	12 M.,	17.31	atmospheres.
"	1 P.M.,	21.72	"
"	3.15 "	26.04	"
"	4.00 "	26.74	"
"	5.00 "	27.51	"
"	5.25 "	28.11	"

At 5.40 P.M. the porcelain tube burst. The last reading corrected for temperature gave a pressure of 27.63 atmospheres at 19°.6.

10. Resistance of the membrane, 54,000 ohms. Cell set up at 5.40 P.M. The following readings were obtained:

Pressure at	5.55 P.M.,	12.43	atmospheres.
"	6.20 "	19.65	"
"	6.40 "	20.83	"
"	6.50 "	21.68	"

At 7.00 P.M. the glass tube was shattered.

11. Resistance of the membrane not exactly known, but over 200,000 ohms. Solution of sugar N/100 with respect to potassium ferrocyanide, and the water in which the cell was immersed N/100 with respect to copper sulphate. The solution of sugar fresh and free from invert sugar. Cell set up at 5 P.M. Pressure at 5.10 P.M., 7.89 atmospheres; at 6.45 P.M., 31.41 atmospheres (corrected). Temperature 24°.9. Shortly after the second reading the glass tube was shattered.

It is probable that all of the solutions which remained in the cells more than twenty-four hours were slightly inverted, but whether the reaction had proceeded in any case to an extent which materially affected the osmotic pressure of the solution is not known. This is a matter which must be carefully investigated when accurate measurements are attempted. Our sugar solutions were prepared from the purest obtainable "rock candy," and when first made up, they did not reduce Fehling's solution.

We conclude from the results recorded above that the osmotic pressure of a half-normal solution will be found to lie between 13 and 14 atmospheres at temperatures in the neighborhood of 20°, and probably between 13.4 and 13.8 atmospheres. And it is certain from the last experiment with normal solutions (No. 11) that the pressure of a normal solution

of sugar is not less than 31.4 atmospheres. The solution in this case was fresh and free from invert sugar, and the highest pressure was reached within two hours after the solution had been made. During so short an interval no appreciable inversion could have occurred. In other words, the whole observed pressure was undoubtedly due to molecules of cane sugar.

The divergence of the pressure of a half-normal solution (if it is found to be between 13 and 14 atmospheres) from the theoretical value is interesting in connection with the abnormal freezing-point of a sugar solution of the same concentration. If the osmotic pressure of a half-normal solution of sugar deviates in the same degree from the theoretical as does the freezing-point, the pressure should be about 13.5 atmospheres.[1] A similar divergence from the theoretical value on the part of a normal solution of sugar would give for it an osmotic pressure of about 33 atmospheres, that is, about 1.5 atmospheres above the pressure reached in our last experiment, in which the pressure had pretty certainly not reached its maximum when the cell was shattered.

The evolution of the cell has now reached the point where we think it admissible for us to undertake a more careful determination of osmotic pressure, and we shall, in the immediate future, attempt to ascertain with a much greater degree of exactness the pressure of half-normal and normal solutions. The measurement of the pressures of solutions of intermediate and lower concentrations will be undertaken by others working in this laboratory. We shall also attempt to make membranes by the electrolytic process from other substances than copper salts and ferrocyanides, and to ascertain how far electrolytically prepared membranes may be utilized for the study of the dissociation of electrolytes. In the meantime we shall endeavor to improve the cell. Very much remains to be learned with regard to the conditions which are favorable or unfavorable to the production of a perfect membrane. So far as we know, we have produced the ideal membrane in one instance only; namely, in the case of the last experiment, when the membrane almost ceased to permit the passage of the cur-

[1] Jones: Ztschr. phys. Chem., 12, 642.

rent and exhibited such astonishing efficiency that the pressure rose to over 31 atmospheres in less than two hours. It is possible, however, that we have had equally good membranes on other occasions and that their failure to work as well was due to faults not inherent in the membranes themselves. It is of the utmost importance to ascertain the conditions under which such a membrane as our last one can be produced at will.

The difficulties of construction are by no means completely overcome, and we have in view a number of changes which we hope will prove of advantage. That these difficulties are of great magnitude will be realized if one considers that in our last experiment the pressure which was measured and which was still below what we were called upon to control would suffice to raise a column of water at 20° to a point 15 meters higher than the top of the Eiffel tower, or which would raise from its base a marble shaft whose height is 120 meters. These comparisons will perhaps make it clear that the most painstaking attention to every detail of construction is absolutely essential to success when an apparatus like ours is to be made up of several parts, consisting of different materials, and which must be united without the usual mechanical means of securing strong joints.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
June, 1902.

A REDETERMINATION OF THE ATOMIC WEIGHT OF LANTHANUM.

BY HARRY C. JONES.

A number of determinations of the atomic weight of lanthanum have already been made. The more important and reliable are the following:

Rammelsberg[1] precipitated the sulphuric acid in lanthanum sulphate as barium sulphate. He found the atomic weight of lanthanum, from one determination, to be 133.4.

In the same year Choubine[2] published determinations of the atomic weight of lanthanum. He transformed the oxide into

[1] Pogg. Ann., **55**, 66 (1842).
[2] J. prakt. Chem., **26**, 443 (1842).

lanthanous chloride and then precipitated the chlorine by means of silver nitrate. The two determinations gave values lower than that found by Rammelsberg, but Choubine's material was almost certainly contaminated with other substances.

The same criticism applies to the work of Hermann,[1] who, the following year, made a few determinations of the atomic weight of lanthanum.

The first determination of the atomic weight of lanthanum upon which much stress can be laid is that of Marignac.[2] He titrated solutions of lanthanum sulphate with a solution of barium chloride. As a mean of nine determinations he found the atomic weight of lanthanum to be 140.2.

Holzmann[3] attempted to determine the atomic weight of lanthanum by several methods. He analyzed the sulphate by precipitating the lanthanum as oxalate, igniting the oxalate, and weighing the oxide. From three determinations he obtained for the atomic weight of lanthanum the value 138.8. He also analyzed the iodate of lanthanum by precipitating the lanthanum as oxalate and determining the iodic acid volumetrically. The lower values found by this method cannot be regarded as important, since the method has been shown to be defective. Holzmann also determined the atomic weight of lanthanum by analyzing the double nitrate of lanthanum and magnesium ($2La(NO_3)_3.3Mg(NO_3)_2.24H_2O$). This method, like that involving the use of the iodate, is open to serious objection.

In 1860 Czudnowicz[4] published one analysis of lanthanum sulphate, and a year later Hermann[5] analyzed both the sulphate and carbonate of lanthanum. Since the material was not purified with sufficient care, no stress can be laid upon the results obtained.

In 1868 Zschiesche[6] freed his lanthanum from didymium and made six analyses of lanthanum sulphate. The values

[1] J. prakt. Chem., **30**, 199 (1843).
[2] Arch. Sci. Phys. et Nat., [1], **11**, 29 (1849).
[3] J. prakt. Chem., **73**, 343 (1858).
[4] *Ibid.*, **80**, 33 (1860).
[5] *Ibid.*, **82**, 395 (1861).
[6] *Ibid.*, **104**, 176 (1868).

found for the atomic weight of lanthanum differ more than three units. The mean value is 135.9.

Erk[1] analyzed the sulphate of lanthanum by precipitating the lanthanum with ammonium oxalate, igniting the oxalate and weighing the oxide. The mean of three determinations gave for the atomic weight of lanthanum the value 135.5.

Erk also determined the sulphuric acid in the filtrates and from these results calculated the atomic weight of lanthanum to be 135.3.

Marignac[2] redetermined the atomic weight of lanthanum by further purifying the sulphate by repeated crystallization. In two determinations the sulphate was heated to dull redness, weighed, and then heated to a white heat to convert the sulphate into oxide. In two other determinations the dried sulphate was dissolved and the solution treated with a solution of ammonium oxalate. The oxalate of lanthanum was strongly heated to convert it into the oxide, and the oxide weighed. By the first method Marignac obtained for the atomic weight of lanthanum the value 138.9; by the second method the value 138.7.

Clève[3] made five determinations of the atomic weight of lanthanum in 1874. The oxide, analyzed spectroscopically, was dissolved in nitric acid. The solution was treated with sulphuric acid, evaporated to dryness, and the residue heated to remove all excess of sulphuric acid. The amount of sulphate formed was then weighed. The mean of Clève's determinations gave, for the atomic weight of lanthanum, the value 139.3.

Brauner[4] made his first determinations of the atomic weight of lanthanum in 1882. In two syntheses of the sulphate from the oxide he obtained for the atomic weight of lanthanum the values 138.94 and 138.83, the mean being 138.88.

In a second series of determinations published in the same year, Brauner[5] obtained considerably lower values. With this material, which Brauner thinks was purer than that originally

[1] Ztschr. Chem., N. F. **7**, 106; Ztschr. anal. Chem., **10**, 509 (1871).
[2] Ann. chim. phys., [4], **30**, 68 (1873).
[3] K. Svensk. Akad. Handlingar, **2**, 7 (1874).
[4] Monatsh. Chem., **3**, 28 (1883).
[5] *Ibid.*, **3**, 493.

used, he obtained values for the atomic weight of lanthanum ranging from 138.06 to 138.45, with a mean of 138.28.

Clève[1] published his second series of determinations of the atomic weight of lanthanum in 1883. The material which Clève used was unquestionably purer than any which had been employed up to that time. He made a series of twelve determinations by converting the oxide into the sulphate. The atomic weight of lanthanum calculated by Clève on the basis of $SO_3 = 80$ varied from 138.07 to 138.35, with a mean of 138.22. Calculated on the basis of the present values for oxygen and sulphur, this becomes 138.55. Of all the determinations of the atomic weight of lanthanum thus far made, this is apparently entitled to the greatest confidence.

Bauer,[2] in 1890, made four determinations of the atomic weight of lanthanum by converting the oxide into the sulphate. The results calculated in terms of oxygen = 16 and sulphur = 32.06 range from 138.91 to 138.3.

Bettendorff[3] made four determinations of the atomic weight of lanthanum by the same method, *i. e.*, the synthesis of the sulphate from the oxide. He calculated the atomic weight of lanthanum on the basis of O = 15.96, S = 31.98, and obtained values ranging from 138.21 to 138.24. His results calculated on the present basis, of oxygen = 16 and sulphur = 32.06, give as the atomic weight of lanthanum the value 138.62.

Wolcott Gibbs[4] carried out, in 1893, an extensive investigation on the rare earths, with special reference to methods of separating and determining these substances. He analyzed the colorless nitrate of ammonium and lanthanum furnished him by Dr. Shapleigh, by precipitating the lanthanum as oxalate and igniting the oxalate. He found for the atomic mass of lanthanum the value 139.7.

Gibbs does not seem to lay much stress upon this result as a determination of the atomic weight of lanthanum, since his work was carried out rather to test certain analytical methods

[1] Bull. Soc. Chim., **39**, 151 (1883).
[2] Dissertation, Freiburg (1884).
[3] Ann. Chem. (Liebig), **256**, 168 (1890).
[4] Proc. Am. Acad., **28**, 260 (1893).

than to purify the several elements and determine their atomic weights. Gibbs states[1] that Shapleigh found values of the same order of magnitude as his own by means of the sulphate method.

The most recent determination of the atomic weight of lanthanum is that of Brauner and Pavliček.[2] The material was purified by crystallizing the double nitrate of ammonium and lanthanum. It was then fused with potassium sodium nitrate and fractionally precipitated with potassium hydroxide. Brauner determined the atomic weight of the lanthanum in the several fractions and found it to vary from 138.78 in the most positive fraction to 139.1 in the most negative. They regard the most positive fraction as representing the purest lanthanum. They, however, think that since the sulphate is hygroscopic, from 0.2 to 0.3 should be added to the value found by experiment. When this is added to 138.78 they obtained 139.0, which they regard as the true atomic weight of lanthanum.

Brauner and Pavliček conclude that the sulphate method of determining atomic weights, as ordinarily applied, is unreliable, since the sulphate always contains acid sulphate. They used the sulphate method, but determined the amount of acid sulphate present by titrating with sodium hydroxide and introducing the corresponding correction.

This conclusion, we shall show, is not based upon a sufficient study of the facts. The presence or absence of acid sulphate depends upon the temperature to which the sulphate has been heated.

It is obvious, from the above sketch of what has been done, that the question of the atomic weight of lanthanum is far from settled. Take even the more recent and trustworthy determinations, and we find a lack of concordance amounting to several units. A careful study of these investigations will show that this is probably due to the different degrees of purity of the materials employed.

[1] Proc. Am. Acad., **28**, 262 (1893).
[2] Proc. Chem. Soc., **17**, 63.

Material Used.

The present investigation would not have been undertaken but for the fact that an unusually pure specimen of lanthanum was placed at the writer's disposal by Dr. Waldron Shapleigh, just before his death.

I should like to take this opportunity to express my many obligations to Dr. Shapleigh, in connection with the work already done on the atomic weights of the so-called "rare earths." He isolated lanthanum, praseodymium, neodymium, thorium, and cerium on a scale never dreamed of before his time, and placed the fruit of a score of years at the disposal of those who desired to carry out purely scientific investigations, with a liberality which is rare. Scientific, as well as technical, chemistry, has suffered an irreparable loss by the death of this most genial man.

In addition to having at my disposal remarkably pure ammonium lanthanum nitrate by the kilogram, the unusual spectroscopic facilities offered by the physical department of this university, in the Rowland spectroscope, made it highly desirable that the atomic weight of lanthanum should be carefully studied.

The double nitrate of ammonium and lanthanum was subjected to fractional crystallization until spectrum analysis showed that it was homogeneous and contained as impurity only a trace of cerium. The double nitrate was heated in small quantities over the blast-lamp until only the oxide of lanthanum remained.

To remove any trace of the nitrate which might not have been decomposed, the resulting oxide was boiled for a considerable time with water which had been purified by the method described by Jones and Mackay[1] for preparing water for conductivity measurements. Indeed, all the water used in this work was purified by this method.

The oxide was filtered off and thoroughly washed with hot water. It was then treated with hot, dilute nitric acid, and dissolved, leaving, however, a slight cloudiness, which was basic cerium nitrate. The solution was then filtered repeat-

[1] This JOURNAL, 19, 91 (1897).

edly through the same filter until it was perfectly clear.

The solution of the nitrate was then treated with a dilute solution of oxalic acid, which had been purified as follows: Commercial oxalic acid was dissolved in redistilled, cold water. The solution was concentrated by evaporation and crystals of the acid obtained. The crystals were then dissolved in a mixture of equal parts of pure, anhydrous ethyl alcohol and pure, anhydrous ether. In this way the oxalic acid was freed from every trace of metallic salts.

To the solution of the oxalic acid in alcohol and ether 3 to 4 volumes of water were added and the mixture boiled for some time, until the ethyl oxalate formed had been decomposed. The solution was then evaporated and the oxalic acid allowed to crystallize.

The oxalate of lanthanum was precipitated from the nitrate in the presence of nitric acid. In this way it was separated from all of the more common impurities, such as calcium, iron, etc.

The oxalate was then decomposed to the oxide and analyzed spectroscopically by Mr. L. E. Jewell, whose work in this field is so well known. The only impurity which could be detected was a trace of cerium, and this was not more, and probably much less, than 0.01 per cent.

The oxalate was again decomposed to the oxide, the oxide dissolved in hot, dilute nitric acid, and the lanthanum precipitated again as the oxalate. The oxalate was decomposed over the blast-lamp and the resulting oxide used for the following determination:

To determine whether the oxide prepared in this way contained any oxide richer in oxygen than the sesquioxide, a specimen was heated in an atmosphere of hydrogen. The oxide was placed in a porcelain boat and the whole weighed. The boat was shoved into a hard-glass tube and the tube heated in a combustion-furnace until the glass began to soften; a stream of hydrogen, purified by passing through solutions of sodium plumbate and silver nitrate, and dried, being led through the tube. After the oxide had been heated to redness for about an hour it was allowed to cool in an at-

mosphere of hydrogen, and then placed in a desiccator over phosphorus pentoxide until weighed. No loss in weight could be detected. The oxide was then returned to the glass tube and reheated for a second hour in an atmosphere of hydrogen. It maintained perfectly constant weight. From these experiments the conclusion was drawn that the oxide of lanthanum prepared by decomposing the oxalate is the pure sesquioxide, free from any higher oxide.

Carrying Out a Determination.

The glaze was removed from the inside of a porcelain crucible by treating it with hydrofluoric acid, and the resulting dust brushed out with the greatest care. Indeed, the crucible was scoured with a button-brush turned in a lathe, until every particle of loose material had been removed. This was done to prevent the oxide of lanthanum from coming in contact, while hot, with the glaze on the crucible and the possible formation of a silicate of lanthanum. The glaze was not removed from the exterior of the crucible, since its presence prevented any reducing gases from the flame from passing through the porcelain and coming in contact with the oxide.

The desired amount of lanthanum oxide was placed in the porcelain crucible and heated over the blast-lamp to constant weight.

A platinum crucible was placed in a weighing tube with a ground-glass stopper and weighed. The oxide of lanthanum was quickly transferred from the porcelain crucible, in a desiccator containing phosphorus pentoxide, to the platinum crucible. The latter was quickly introduced into the weighing tube and the whole reweighed. In this way the weight of the oxide used in an experiment was determined.

The weighings were made to 0.00005 gram. The writer is of the opinion that this is sufficiently accurate for refined atomic weight determinations, since every chemist is fully aware that the most accurate operation carried out in a chemical laboratory is the weighing with a satisfactory balance. The weighings were made to 0.05 milligram, and the 0.1 milligram nearest to the value found was taken as the true

weight. The error in weighing was thus quite as small as in the remaining operations connected with the carrying out of the method.

The oxide was then treated with a measured volume of fairly concentrated sulphuric acid and warmed very gently until it had been transformed into the sulphate. Unless this precaution is taken the reaction is liable to take place with some violence and cause the substance to spatter upon the sides and top of the crucible. The sulphate was then evaporated slowly to dryness in an upright air-bath, the crucible resting upon a porcelain triangle about 2 cm. from the bottom of the bath. The sulphate was then heated sufficiently high to decompose all acid sulphates which might have been formed. It was then reheated until constant weight was established.

Proof of the Absence of Acid Sulphates.

The question of the presence of acid sulphates of lanthanum was studied with care, especially since Brauner[1] had stated that under these conditions Wyrouboff's acid sulphate was always present. Indeed, Brauner and Pavliček determined the amount of the acid sulphate present under the conditions with which they worked by titration with sodium hydroxide.

The sulphate of lanthanum which had been heated to constant weight was at first treated with a few drops of a solution of ammonium carbonate and reheated. It lost in weight very considerably and continued to do so as more and more ammonium carbonate was added. This led to the conclusion that the lanthanum sulphate was undergoing decomposition in the presence of ammonium carbonate, giving rise to lanthanum carbonate, and ammonium sulphate which was volatilized at the temperature employed. This was proved by the fact that when the lanthanum sulphate was dissolved in water a very considerable insoluble residue remained behind. Indeed, this is just what we would expect when we consider that lanthanum is such a weak base. This is the probable explanation of the fact pointed out by Brauner and Pavliček

[1] Proc. Chem. Soc., 17, 63; Centrbl., 1901, 1035.

that when ammonium carbonate was added to lanthanum sulphate, which had been heated to 450°, a further loss in sulphuric acid took place.

The method of testing for the presence of acid sulphate was the following: The sulphate was heated to constant weight and dissolved in water. The solution was perfectly clear, showing that none of the sulphate had been decomposed. The solution was then tested to see whether it would show an acid or basic reaction. In every determination the solution of the sulphate was found to be perfectly neutral, showing not the slightest trace of acid or basic properties.

These facts, together with the complete solubility of the sulphate, show that we had to deal with the normal sulphate, free from both acid and basic salt.

A volume of the sulphuric acid just equal to that used in each determination was evaporated to dryness and the residue weighed. The residue was found to weigh 0.00002 gram.

The Results.

Twelve determinations were completed by the method described above, and the results are given below, calculated on the basis of oxygen = 16, sulphur = 32.06. These include every determination which was completed. A few determinations were lost by accident, especially in the earlier stages of the work, due to the spattering of the sulphate upon the lid of the crucible. These determinations were interrupted as soon as any spattering was discovered, and the resulting sulphate was not weighed.

	La_2O_3.	$La_2(SO_4)_3$.	$3SO_3 = 240.18$.	At. wt. La.
I.	1.0122	1.7592	0.7470	138.72
II.	1.1268	1.9581	0.8313	138.78
III.	0.94585	1.6437	0.69785	138.77
IV.	1.0675	1.8553	0.7878	138.73
V.	0.9030	1.5692	0.6662	138.78
VI.	1.1273	1.9589	0.8316	138.79
VII.	0.9407	1.6347	0.6940	138.78
VIII.	1.0455	1.8168	0.7713	138.78
IX.	1.1271	1.9586	0.8315	138.78
X.	1.3074	2.2720	0.9646	138.77
XI.	1.3389	2.3267	0.9878	138.77
XII.	1.2012	2.0874	0.8862	138.78

Taking the mean of the twelve determinations, we have for the atomic weight of lanthanum the value 138.77.

Attempt to Use the Oxalate Method.

An attempt was made to determine the atomic weight of lanthanum by decomposing the oxalate of lanthanum to the oxide, or by determining the oxalic acid in the oxalate by titration with a standard solution of potassium permanganate. This method had to be abandoned on account of the nature of lanthanum oxalate. It was found to be practically impossible to obtain lanthanum oxalate under conditions where it would give constant weight. The oxalate continued to lose in weight when dried for several days at 110; it further lost in weight when dried at 150°, and still further loss in weight was sustained when it was heated to 190°. A specimen which had been dried for a week at 190° gave off a very considerable quantity of water when heated from 230° to 240°, showing that considerable water had been retained by the oxalate above 200°.

The decomposition temperature of lanthanum oxalate was then studied. The salt was placed in a glass tube closed at one end and connected at the other with a wash-bottle closed by means of a ground-glass stopper. A solution of barium hydroxide was introduced into the bottle and protected from the carbon dioxide in the air by connecting it with a second similar bottle containing a solution of sodium hydroxide. Any carbon dioxide escaping from the decomposing oxalate was thus conducted through the solution of barium hydroxide. The oxalate was found to show incipient decomposition at 250°, which became very marked at somewhat higher temperatures.

Since the oxalate continued to give off water so close to its decomposition temperature it was not safe to completely dehydrate the salt and weigh it for the purpose of an atomic weight determination. The oxalate method for determining the atomic weight of lanthanum was, therefore, abandoned.

The result of the above investigation is, then, to show that

the atomic weight of lanthanum is 138.77 on the basis of oxygen = 16.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1902.

Contribution from the Chemical Laboratory of the Nebraska Wesleyan University.

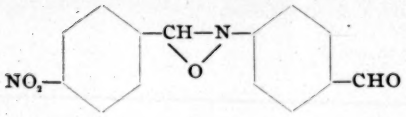
I. ON *p*-AZOXYBENZALDEHYDE.

BY F. J. ALWAY.

Kirpal[1] has shown that when nitrobenzaldehyde, dissolved in boiling water, is treated with zinc dust a yellowish-green solution results. From this solution he was unable to isolate the *p*-hydroxylaminebenzaldehyde, whose formation was to be expected in this case. This solution soon became turbid from the separation of a reddish-yellow solid. He found the completion of the change to be accelerated by blowing air through the solution, which was at the same time kept warm. This substance, when purified by recrystallization, melted at 194° and contained two aldehyde groups. As the elementary analysis and the molecular weight determination agreed with the formula of *p*-azoxybenzaldehyde and as Bamberger had shown that in many analogous cases aromatic hydroxylamines pass readily into the corresponding azoxy compounds the proof of the correctness of the above formula was considered sufficient. Had not Lucius and Brüning[2] recently patented a process for the preparation of *p*-azoxybenzaldehyde by another method which gave a substance differing in properties from that described by Kirpal, it would not have been considered necessary to further investigate the constitution of the compounds obtained by Kirpal's method as well as by the other.

While Bamberger, with his students (including Kirpal), was studying the various classes of *p*-hydroxylamine derivatives, Gatterman was investigating the electrolytic reduction, in concentrated sulphuric acid, of the aromatic nitro compounds. He found that when the primary reduction-product of *p*-nitrobenzaldehyde, *viz.*, N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime[3] was oxidized by ferric chloride solution, there

[1] Ber. d. chem. Ges., **30**, 1597.
[2] Patentblatt, **21**, 894; D. R. P., 111,384.
[3] Ber. d. chem. Ges., **29**, 3037.



was formed *p*-nitrobenzaldehyde, together with a substance melting at 190° and not volatile with steam, and that the same non-volatile compound was produced when the above benzaldoxime was heated with dilute acids and the product distilled with steam. In both cases *p*-nitrobenzaldehyde was carried over by the steam.

Gattermann would have regarded this non-volatile substance as *p*-azoxybenzaldehyde had not Kirpal assigned to this latter compound a melting-point 4° higher (*viz.*, 194°). As the method of preparation used by Kirpal, viewed in the light of Bamberger's research on the oxidation of hydroxylamines to azoxy compounds when exposed to the air, seemed to fully identify the compound melting at 194° as *p*-azoxybenzaldehyde, Gattermann suggested that the compound melting at 190° might be the anhydride of *p*-hydroxylaminebenzaldehyde, *viz.*, $O(NH.C_6H_4.CHO)_2$.

Lucius and Brüning obtained the compound patented by them under the name of *p*-azoxybenzaldehyde (m. p. 180°) by the decomposition of its anilide (m. p. 167°), which, in turn, was produced by the treatment of *p*-nitrobenzylaniline with caustic alkalies.

If the compound obtained by the last method had the structure assigned to it, the compounds of Gattermann and Kirpal would probably be identical and both be a hydroxylamine anhydride, representing a new class of compounds. As will be seen from the calculated percentages and molecular weights given below, neither an elementary analysis nor a molecular weight determination would decide between the two formulæ, especially when the lowest percentage of hydrogen found in any analysis was 4.29 (Kirpal) and when the percentage of carbon was found, in all analyses, less than 66.00.

	Calculated for *p*-azoxybenzaldehyde, $C_{14}H_{10}O_3N_2$.	Calculated for the hydroxylamine anhydride, $C_{14}H_{12}O_3N_2$.
Molecular weight	254.0	256.0
C	66.1	65.6
H	3.9	4.7
N	11.0	10.9

In the hope of identifying *p*-azoxybenzaldehyde with one of the three above-mentioned compounds, a careful investigation of the subject has been undertaken in this laboratory. The results of my experimental work, up to the present, may be summarized as follows: The compound, described by Kirpal as *p*-azoxybenzaldehyde, melting at 194°, is identical with that mentioned by Gattermann, and when pure melts at 190° uncorr. Throughout the present article the name "*p*-azoxybenzaldehyde" is used to designate the compound melting at 190°, although the proof of its nature is not yet fully established. In addition to methods already published,[1] it may be obtained without difficulty by treating the secondary reduction-product of *p*-nitrobenzaldehyde with dilute acids or with ferric chloride solution, the yield being much greater than when the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime is similarly treated. The last-mentioned compound, when treated with phenylhydrazine, yields the corresponding hydrazone, which readily reacts with more phenylhydrazine to form the hydrazones of *p*-nitrobenzaldehyde and *p*-azoxybenzaldehyde. The latter hydrazone is also formed by the action of phenylhydrazine upon *p*-nitrosobenzaldehyde. The formation of *p*-azoxybenzaldehyde by Kirpal's method depends upon the presence of oxygen and is favored by the presence of alkalies. It forms with aniline an anilide, with fuming nitric acid a mononitroazoxybenzaldehyde, and with phosphorus pentachloride an azoxybenzalchloride. When warmed with concentrated sulphuric acid to 100° it undergoes no change. Ordinary concentrated nitric acid, benzoyl chloride, acetyl chloride, acetic anhydride, and nitrous acid are without action upon it. The secondary reduction-product of *p*-nitrobenzaldehyde[2] is formed also by the electrolytic reduc-

[1] Ber. d. chem. Ges., **29**, 3037; **30**, 1597.
[2] *Ibid.*, **29**, 3037.

tion of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime. In this case a nitro compound is evidently reduced, in acid solution, to an azoxy compound. The action of aniline upon the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime and upon *p*-nitrosobenzaldehyde gives hydrazo and azo derivatives respectively, and not azoxy compounds. *p*-Nitrosobenzaldehyde, unlike the *p*-nitroso compounds investigated by Bamberger,[1] is changed by concentrated sulphuric acid into a polymeric compound.

EXPERIMENTAL.

Electrolytic Reduction of p-Nitrobenzaldehyde.

The exact conditions of reduction given by Gattermann[2] were followed. The *p*-nitrobenzaldehyde was dissolved in concentrated sulphuric acid and subjected to the action of a current of 6 volts and 2 to 3 amperes. The progress of the reaction was determined at frequent intervals by pouring a small quantity of the sulphuric acid solution into ice-water, filtering out the precipitate, which varied in color from yellow to red, thoroughly washing this on the filter with ice-water, in order to remove all adhering acid, and then, by the use of water and of pyridine, isolating the different compounds contained in the precipitate. Alcohol may not be used to extract the *p*-nitrobenzaldehyde as the primary reduction-product is soluble in the alcoholic solution of this aldehyde. Boiling water dissolves the unchanged aldehyde, while boiling pyridine dissolves the primary reduction-product. The red, secondary reduction-product remains after treatment with pyridine. At the end of about ten hours' further reduction, the primary product had entirely disappeared, and there remained only the red substance. When the pure primary product, recrystallized from pyridine, was subjected to further reduction under the conditions given above, it was likewise completely changed into the red substance in about ten hours.

[1] Ber. d. chem. Ges., **31**, 1513.
[2] *Ibid.*, **29**, 3037.

The Secondary Reduction-Product of p-Nitrobenzaldehyde.

The red substance does not melt below 330°, but seems to undergo decomposition at 220° to 230°. It is insoluble in the ordinary organic solvents and also in carbon disulphide, nitrobenzene, pyridine, phenol, and naphthalene. It dissolves in concentrated sulphuric acid, from which it may be recovered by pouring the solution into ice-water. When this solution is warmed to 100° the dissolved substance remains unchanged; but, when water is added to this warm solution, it is decomposed, yielding *p*-azoxybenzaldehyde. When boiled for half an hour with dilute sulphuric or hydrochloric acid, or for three hours with glacial acetic acid, the same compound is formed. By oxidation with ferric chloride solution, *p*-nitrosobenzaldehyde and *p*-azoxybenzaldehyde are produced. No trace of *p*-nitrobenzaldehyde could be detected.

The oxidation of 1 gram of the primary reduction-product yielded 0.6 gram *p*-nitrosobenzaldehyde, 0.03 to 0.1 gram *p*-azoxybenzaldehyde, and 0.2 gram *p*-nitrobenzaldehyde. The small quantity of the last is probably due to the fact that it is appreciably soluble in cold water. The oxidation was effected by adding ferric chloride solution to the primary reduction-product suspended in water, while a rapid current of steam was led into the mixture. The *p*-azoxybenzaldehyde remained in the flask, suspended in the water. The *p*-nitrobenzaldehyde and the *p*-nitrosobenzaldehyde were carried over by the steam and collected in the receiver. The contents of the receiver were cooled, the flocculent precipitate filtered out, dried, and recrystallized from glacial acetic acid. The *p*-nitrosobenzaldehyde separated out completely when the solution was cooled, while the *p*-nitrobenzaldehyde remained dissolved.

The nitrosobenzaldehyde was filtered out and to the filtrate cold water was added in excess. Pure *p*-nitrobenzaldehyde separated out rapidly. Oxidation of 1 gram red reduction-product yielded 0.5 to 0.6 gram azoxybenzaldehyde and 0.25 to 0.35 gram *p*-nitrosobenzaldehyde. The distillate in this case, after the nitrosobenzaldehyde had been filtered out, was

extracted with ether. No trace of *p*-nitrobenzaldehyde was isolated from either the precipitate or the filtrate.

As no solvent was found from which it could be recrystallized, no analysis of the substance was made.

p-Azoxybenzaldehyde, $ON_2(C_6H_4.CHO)_2$.—This aldehyde has been obtained from three different compounds, the primary reduction-product, the secondary reduction-product, and *p*-nitrosobenzaldehyde, as well as by Kirpal's method described above.

p-Nitrosobenzaldehyde and the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime, when treated with phenylhydrazine, yield the hydrazone (see below) of the above aldehyde.

The solid remaining suspended in the water when the reduction-product of *p*-nitrobenzaldehyde was digested with dilute acid, or oxidized by ferric chloride solution, was filtered out and dried. In this condition it had a slight tinge of red. It was recrystallized from acetic acid after boiling several times with animal charcoal. It melted at 190°. It was then recrystallized from benzene four times. The melting-point remained constant. It crystallized in long, yellow needles from benzene or from dilute acetic acid. It is slightly soluble in hot water, cold alcohol, and ligroin, more soluble in boiling ligroin; it is readily soluble in benzene and glacial acetic acid, from which it crystallizes on cooling.

	Calculated for $C_{14}H_{10}N_2O_3$.	Found.
N	11.02	11.11

The molecular weight was determined by the freezing-point method, using naphthalene as the solvent.

	Calculated.	Found.	
Molecular weight	254	256	258

When boiled with dilute sulphuric or hydrochloric acid for three hours, it remained unchanged. It underwent no change when the solution in concentrated sulphuric acid was warmed to 100°, when boiled with ordinary concentrated nitric acid, with acetyl chloride or with benzoyl chloride, or when heated in a sealed glass tube with acetic anhydride to 100° for one hour. By oxidation with chromic acid in glacial acetic acid

solution, a gray substance, insoluble in ordinary solvents, was formed. This was not further investigated. It is doubtless *p*-azoxybenzoic acid, described by Kirpal.[1] When treated with zinc dust and acetic acid the *p*-azoxybenzaldehyde yields red crystals. Similar red crystals were observed at times among the yellow crystals obtained by recrystallizing the crude *p*-azoxybenzaldehyde, prepared as above described, from 90 per cent acetic acid. These have not yet been further investigated.

Preparation of p-Azoxybenzaldehyde by Kirpal's Method.[2]

As the melting-point of the aldehyde described by Gattermann remained constant at 190°, I prepared it by Kirpal's method, applying the results of Bamberger's investigation of the action of alkalies upon arylhydroxylamines in the presence of oxygen.[3]

Two grams of *p*-nitrobenzaldehyde were added to 150 cc. boiling water, and after one minute 12 grams zinc dust were added. The mixture was kept gently boiling for five minutes and then filtered under suction, using a Büchner funnel. The filtrate was placed in a stoppered flask and quickly cooled. A copious yellow precipitate separated out. This was found to be *p*-nitrobenzaldehyde, together with a little *p*-azoxybenzaldehyde. The greenish-yellow filtrate rapidly became turbid, and when air was passed through it a reddish-yellow precipitate formed. The reaction was complete at the end of twenty to twenty-four hours at 20°, and at the end of two to four hours when the temperature was kept between 90° and 100°. When the air was freed from acids (hydrochloric acid being present in greater or less degree in the air of a chemical laboratory), by first passing through wash-bottles containing potash solution and then through two containing distilled water to prevent any alkali solution being mechanically carried over, the precipitate was light-yellow in color with no trace of red. When the air was first passed through concentrated sulphuric acid, but not through alkaline solution, the precipi-

[1] Ber. d. chem. Ges., 30, 1598.
[2] *Loc. cit.*
[3] *Ibid.*, 33, 118, 271.

tate was reddish-yellow. The addition of acids to the filtrate caused a similar precipitate to form. When sodium hydroxide solution was added to the filtrate a deep-red coloration was produced, while a yellow flocculent precipitate rapidly separated out. When this mixture was kept agitated the reaction was complete at the end of half an hour. The filtered and dried precipitate obtained in the last operation was bright-yellow in color.

In order to determine the influence of the oxygen of the air upon the course of the reaction, the above experiments were repeated in an atmosphere of hydrogen which was purified by passing through a series of six wash-bottles, containing, respectively, potassium permanganate solution, concentrated sulphuric acid, pyrogallic acid in sodium hydroxide, and lastly, boiled distilled water. The liquid containing *p*-nitrobenzaldehyde in suspension was filtered directly into the digestion-flask, and the air in the latter was immediately replaced by hydrogen. The solution showed only traces of turbidity before the air had been expelled from the flask. The hydrogen was kept rapidly bubbling through the yellowish-green solution. After half an hour, at 20°, no appreciable change was noticed. Then the current of hydrogen was replaced by one of air, purified by passing through another set of wash-bottles (potassium permanganate solution, concentrated sulphuric acid, caustic soda solution). A yellow, flocculent precipitate soon began to form. The experiment was repeated (again in an atmosphere of hydrogen), keeping the contents of the digestion-flask boiling. At the end of thirty minutes very little solid had separated out. When sodium hydroxide solution was introduced into the yellowish-green filtrate, it at once became deep-red in color and a small quantity of a light-colored solid separated out in the course of half an hour. Then air was passed through the mixture another half hour. The filtered and dried solid in this case was reddish-yellow in color. The precipitate seems, from the above, to be red only when acids are present or when oxygen is absent.

All the precipitates thus obtained consisted essentially of

p-azoxybenzaldehyde. Those that were light-yellow in color dissolved in ligroin without residue. The others, when heated with this solvent, left a small quantity of red substance. Even after repeated recrystallization from acetic acid, and lastly from benzene, the yellow needles so obtained melted at 190°. The melting-point given by Kirpal (194°) is accordingly 4° too high. As the melting-point of the corresponding hydrazone was given by him as 230°, while I find it to be 228°, the error seems to have been in the thermometer used by him.

The residue of zinc dust remaining in the Büchner funnel, referred to above, was in one case dried and extracted with hot benzene. This filtrate, when treated with ligroin, yielded *p*-azoxybenzaldehyde. In a second case the residue was extracted several times with boiling water. On cooling, the yellow aqueous solution so obtained precipitated a reddish-yellow substance from which *p*-azoxybenzaldehyde and a smaller quantity of another compound, which crystallized from acetic acid in red needles, and melted at 222°, were obtained. The latter compound has not yet been further investigated.

p-Azoxybenzaldehydehydrazone, $ON_2(C_6H_4.CH : N.NHC_6H_5)_2$.—This compound was obtained by the action of phenylhydrazine upon three different aldehydes, *viz.*, *p*-azoxybenzaldehyde, the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime and *p*-nitrosobenzaldehyde. The preparation from the second compound is described below. The preparation, when *p*-azoxybenzaldehyde is used, has already been described by Kirpal.[1] It was obtained from *p*-nitrosobenzaldehyde in the following manner: A mixture of phenylhydrazine and acetic acid was slowly added to a hot solution of the aldehyde in acetic acid. A rapid evolution of nitrogen at once took place, and a red solid separated out. As soon as the evolution of gas had ceased the reaction-mixture was cooled, the precipitate filtered out and washed on the filter with alcohol to remove the excess of phenylhydrazine. Then it was dried on the water-bath and recrystallized from pyridine. When recrystallized from benzene or from pyridine it forms orange-colored leaflets, which melt at 228° when

[1] Ber. d. chem. Ges., 30, 1597.

heated rapidly. When heated slowly the compound undergoes decomposition at about 218° to 225°. While but slightly soluble in boiling pure alcohol, it dissolves to a considerable extent if the hydrazone of *p*-nitrobenzaldehyde is present.

An analysis was made of a portion of that obtained from the *p*-azoxybenzaldehyde.

	Calculated for $C_{28}H_{22}ON_6$.	Found.
N	19.3	19.2

A complete analysis was made of that obtained from *p*-nitrosobenzaldehyde.

	Calculated for $C_{28}H_{22}ON_6$.	Found.
C	71.9	71.6
H	5.1	5.5
N	19.3	19.0

p-Azoxybenzylideneaniline, $ON_2(C_6H_4.CH : N.C_6H_5)_2$. — *p*-Azoxybenzaldehyde was boiled for five minutes with an excess of aniline, the whole forming a clear solution. On cooling, a yellow crystalline substance separated out. This was well washed with ether to remove the unchanged aniline and then recrystallized from benzene. It forms large, yellow leaflets, melting at 185° to 192°. The melting-point, after repeated recrystallization, was no more definite. It dissolves with difficulty in ether, alcohol, ligroin, and cold benzene, but readily in the last solvent when hot.

	Calculated for $C_{28}H_{20}N_4O$.	Found.
N	13.8	13.8

Nitro-p-azoxybenzaldehyde, $O\begin{cases} N{-}C_6H_4{-}CHO \\ | \\ N{-}C_6H_3{<}\begin{matrix} CHO \\ NO_2 \end{matrix} \end{cases}$ — *p*-Azoxybenzaldehyde was heated with fuming nitric acid until the evolution of brown vapors began. The solution was cooled and precipitated by water. The yellow precipitate was filtered out and recrystallized from glacial acetic acid. It forms yellow needles, melting at 171° to 172°. It is insoluble in water, but slightly soluble in ether and cold alcohol, and

readily soluble in hot acetic acid, from which it crystallizes on cooling.

	Calculated for $C_{14}H_9O_3N_3$.	Found.
N	14.0	13.9

p-Azoxybenzal Chloride, $ON_2(C_6H_4.CHCl_2)_2$.—The finely divided *p*-azoxybenzaldehyde (1 mol.) was mixed in a test-tube with an excess of phosphorus pentachloride (4 mols.). A lively reaction took place, hydrochloric acid escaping and the mass becoming partly liquid. As soon as the violent reaction had subsided the mixture was heated until it formed a clear red solution. This was poured into ice-water, yielding a red precipitate, which was filtered out, washed with water, dried on a porous plate, and recrystallized from ligroin. This compound forms orange-colored leaflets, melting at 115° to 116°.

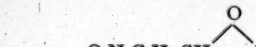
	Calculated for $C_{14}H_{10}ON_2Cl_4$.	Found. I.	Found. II.
N	7.7	7.8	7.8
C	38.9	38.3	38.3

Action of Phenylhydrazine upon the N-p-Formylphenyl Ether of p-Nitrobenzaldoxime.

One gram of the recrystallized reduction-product was mixed with 12 grams absolute alcohol and an excess of phenylhydrazine. This mixture was boiled for one minute. The liquid became red, the yellow reduction-product disappeared, and a red solid took its place. This was filtered out, thoroughly washed on the filter with ether in order to remove the excess of phenylhydrazine, dried, and recrystallized from pyridine. This compound forms dark-red leaflets, melting at 222°. It is insoluble in ether, benzene, acetone, carbon disulphide, and cold alcohol, and slightly more soluble in boiling alcohol and glacial acetic acid. It is readily soluble in boiling pyridine and nitrobenzene, from which it crystallizes on cooling.

	Calculated for $C_{20}H_{18}O_2N_4$.	Found.
N	15.6	15.5

This compound is, accordingly, the hydrazone of the above benzaldoxime derivative, and has the formula



The alcoholic filtrate from the above hydrazone was treated with water. A brown precipitate formed, which was filtered out, dried on the water-bath, and treated with cold benzene. The greater part dissolved in the benzene. The orange-colored residue was filtered out and recrystallized from benzene. It proved to be the hydrazone of *p*-azoxybenzaldehyde. The benzene, with which the crude precipitate had been treated, was evaporated to dryness and the residue recrystallized from glacial acetic acid. The red needles thus obtained were identified as the hydrazone of *p*-nitrobenzaldehyde, melting at 155°.

When aqueous instead of absolute alcohol was used, none, or only traces of the hydrazone melting at 222° was obtained, while there was a good yield of the hydrazones of *p*-nitrobenzaldehyde and *p*-azoxybenzaldehyde.

Anilide of p-Aldehydohydrazobenzene, $C_6H_5.NH.NH.C_6H_4.CH{=}N.C_6H_5$.—The primary reduction-product was heated with excess of aniline until the crackling, produced by the escaping steam, ceased (two to three minutes). On cooling, crystals separated out and the mixture with aniline became solid. This mixture was first washed several times with dilute hydrochloric acid in order to remove the unchanged aniline, then filtered, dried on a porous plate, and lastly boiled with ligroin twice, in order to remove the anilide of *p*-nitrobenzaldehyde. The greater part of the reaction-mixture remained undissolved. The residue was several times recrystallized from benzene.

This compound forms orange-colored leaflets melting at 183° to 186°. It dissolves but slightly in ligroin, alcohol, and acetone, but very readily in hot benzene, from which it separates on cooling.

	Calculated for $C_{19}H_{17}N_3$.	Found.
C	79.4	79.3
H	5.9	5.5
N	14.6	14.3

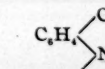
Reaction of p-Nitrosobenzaldehyde with Concentrated Sulphuric Acid.

p-Nitrobenzaldehyde (1 gram) was gradually added to concentrated sulphuric acid (6 cc.), a deep violet-colored solution being formed. After standing ten minutes the solution was poured into ice-water. A red precipitate was at once formed. This was filtered off, thoroughly washed on the filter with water, and then twice recrystallized from glacial acetic acid.

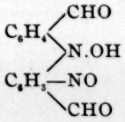
This compound forms a dark-red powder melting at 204° to 206°. It is insoluble in water, ether and ligroin, only slightly soluble in hot benzene, hot alcohol, and cold glacial acetic acid, but readily soluble in the last when hot.

	Calculated for $(C_7H_5O_2N)_x$.	Found.
C	62.2	61.8
H	3.7	3.8
N	10.4	10.3

Bamberger's investigation of the action of concentrated sulphuric acid upon nitrosobenzene and other nitroso compounds,[1] which yield hydroxylamine derivatives of the formula



would have led me to assign the formula



to this compound, had he not found that compounds in which the para-position was occupied by another group or by a halogen atom, were incapable of this aldol condensation.

This compound will be further investigated in this laboratory.

[1] Ber. d. chem. Ges., 31, 1513.

Action of Aniline upon p-Nitrosobenzaldehyde.

Benzeneazobenzylideneaniline, $C_6H_5.N:N.C_6H_4.CH:N.C_6H_5$. —A mixture of aniline (2 mols.), acetic acid (1 mol.), and *p*-nitrosobenzaldehyde (1 mol.) was boiled for a few minutes. The product of the reaction, which solidified on cooling, was twice recrystallized from aqueous alcohol and then once from ligroin. This anilide consists of very small orange-colored needles, melting at 125° to 130°. It is but slightly soluble in cold alcohol, ligroin, and benzene, more readily soluble in boiling ligroin, and very soluble in hot alcohol and benzene.

	Calculated for $C_{19}H_{15}N_3$.	Found.
N	14.7	14.8

Benzeneazobenzaldehyde, $C_6H_4.N:N.C_6H_4.CHO$.—The last-described compound was dissolved in boiling dilute acetic acid. A small quantity of brown oil separated out. The solution was poured off from the oil. On cooling, crystals separated out, which were filtered off and recrystallized from alcohol.

This aldehyde crystallizes from alcohol and from dilute acetic acid in brownish-red, glistening leaflets, melting at 116°. It is but slightly soluble in cold alcohol and ligroin, more soluble in benzene, glacial acetic acid, and hot alcohol.

	Calculated for $C_{13}H_{10}ON_2$.	Found.
C	74.3	74.6
H	4.8	5.0
N	13.3	13.4

The hydrazone of the above aldehyde was prepared by treating the hot solution of the aldehyde in acetic acid with phenylhydrazine. A red precipitate at once appeared, which was recrystallized from glacial acetic acid. It forms long, red needles, melting at 154°.

	Calculated for $C_{19}H_{16}N_4$.	Found.
N	18.7	18.5

The aldehyde, obtained from *m*-nitrobenzaldehyde by methods analogous to those used in the conversion of *p*-nitro-

benzaldehyde into the compound melting at 190°, melts at 129° and yields a hydrazone, melting at 198°. Both this compound and that obtained by the action of caustic alkalies upon *p*-nitrobenzylaniline are still under investigation in this laboratory.

UNIVERSITY PLACE, April 16, 1902.

Contributions from the Chemical Laboratory of the University of Nebraska.

III. A CONTRIBUTION TO THE CHEMISTRY OF THE AROMATIC GLUTARIC ACIDS.

BY S. AVERY.

Vol. XX., p. 509, of this JOURNAL contains an article by Rosa Bouton and the writer "On Phenylglutaric Acid and Its Derivatives." Up to this time only two aromatic glutaric compounds were given in chemical literature, *i. e.*, *β*-phenylglutaric acid[1] and its silver salt. The opening paragraph of this article closes with the words: "We have accordingly entered the study of these acids, hoping to widen our knowledge of the subject in general, and especially to determine the influence of the phenyl groups on melting-points and the formation of anhydrides." The article closes with an account of an unsuccessful attempt to prepare the then unknown *α*-phenylglutaric acid. The closing sentence reads: "We hope to prepare *α*-phenylglutaric acid by another method."

Vol. XX., p. 516, of this JOURNAL contains an article by Mary L. Fossler and the writer, describing a successful attempt to prepare *α*-methyl-*β*-phenylglutaric acid. The closing sentence reads: "We shall investigate this subject further as well as the homologues and isomers of the compounds described."

During the four years that have elapsed since the above was written, the writer and his students have investigated the subjects above outlined. As, however, other investigators have had occasion to enter this field, it seems desirable to publish, without longer delay, the results already obtained. These results are here given in the form of a communication from the writer and his students.

[1] J. prakt. Chem., [2], **38**, 352.

The following table gives the melting-points of the acids, anhydrides, and anilic acids to be found in the literature of the subject:

	Acid.	Anhydride.	Anilic acid.
β-Phenylglutaric	137°.5–138°.5[1]	105°[3]	139°[3]
	138°[2]	105°[4]	139°[4]
	140°[4]		
α-Phenylglutaric	82°–83°[5]	95°[5]	
α-Methyl-β-phenylglutaric	122°[6]	74°[7]	
	125°[7]		
p-Tolylglutaric	165°–167°[8]	153°[8]	194°–196°[8]
β-m-Nitrophenylglutaric	205°–206°[9]	170°.5[10]	160°[10]
	206°[10]		
β-p-Nitrophenylglutaric	236°[11]		120°–121°[12]
	237°[12]	122°.5[12]	
β-o-Nitrophenylglutaric (?)	175°[12]		

EXPERIMENTAL PART.

β-p-TOLYLGLUTARIC ACID.

BY S. AVERY AND H. C. PARMELEE.

The method used in preparing this acid may be outlined as follows:

I. Preparation of p-tolylacrylic ester.

II. Condensation of p-tolylacrylic ester with sodium malonic ester.

III. Saponification in acid solution of the resulting tricarboxylic ester.

p-Methylbenzaldehyde was condensed with acetic ester according to the method of Claisen.[13] The amount of crude ester distilling between 260° and 280° represented 1.175 times the

[1] Michael: J. prakt Chem., [2], **35**, 352.
[2] Vorländer und Kohlmann: Ber. d. chem. Ges., **32**, 1879.
[3] Hermann und Vorländer: Centrbl., 1899, 730.
[4] Avery and Bouton: This JOURNAL, **20**, 509.
[5] Fichter and Mereckens: Ber. d. chem. Ges., **34**, 4175.
[6] Avery and Fossler: This JOURNAL, **20**, 516.
[7] Carter and Lawrence: Chem. News, 1900, p. 253.
[8] Avery and Parmelee: This JOURNAL, **28**, 49.
[9] Knoevenagel: Ann. Chem. (Liebig), **303**, 235.
[10] Avery and Gere: This JOURNAL, **28**, 51.
[11] Knoevenagel: Ann. Chem. (Liebig), **303**, 239.
[12] Avery and Beans: This JOURNAL, **28**, 55.
[13] Ber. d. chem. Ges., **23**, 976.

weight of the aldehyde employed. A small sample, on saponification, yielded nearly pure *p*-tolylacrylic acid, identical in all respects with the acid described by Kröber.[1] The *p*-tolylacrylic ester was condensed with sodium malonic ester and the resulting carboxylic ester saponified with hydrobromic acid. The product of the reaction was extracted with boiling water. On cooling, crystals of *β*-tolylglutaric acid separated out. These were recrystallized first out of a mixture of acetic and petroleum ethers and then out of water. The pure compound forms transparent, oblique prisms, melting at 165° to 167°, soluble in acetic ester, hot water, and chloroform, less soluble in ether, practically insoluble in benzene, petroleum ether, and in water at 0°.

Analysis:

0.2004 gram substance gave 0.4776 gram CO_2 and 0.1192 gram H_2O.

	Calculated for $C_{12}H_{14}O_4$.	Found.
C	64.86	65.01
H	6.35	6.65

Salts of p-Tolylglutaric Acid.

Nearly all the salts described in this paper were formed by precipitation from the ammonium salt.

Silver Salt.—White amorphous powder.

Analysis:

0.2413 gram salt gave 0.1191 gram Ag.

	Calculated for $C_{12}H_{12}O_4Ag_2$.	Found.
Ag	49.46	49.35

Copper Salt.—Green crystalline powder.

Analysis:

0.1627 gram salt gave 0.04279 gram CuO.

	Calculated for $C_{12}H_{12}O_4Cu.H_2O$.	Found.
Cu	21.04	21.08

Calcium Salt.—White crystalline powder.

Analysis:

0.0515 gram salt gave 0.0109 gram CaO.

[1] Ber. d. chem. Ges., 23, 1033.

	Calculated for $C_{19}H_{18}O_4Ca$.	Found.
Ca	15.384	15.118

β-p-Tolylglutaric Anhydride.—This compound may be prepared by heating the acid above its melting-point or by treating the acid with hot acetyl chloride. The latter method is the more convenient. The acetyl chloride is evaporated off on the water-bath and the residue extracted with dry benzene. On the addition of dry petroleum ether to the benzene solution, the anhydride separates out in feathery crystals which melt at 153°.

β-p-Tolylglutaranilic Acid.—The anhydride just described reacts with aniline in benzene solution to form the anilic acid. The acid may be obtained in pure condition by recrystallizing from alcohol. Glistening white needles melted at 194° to 196°. A silver salt of the anilic acid was analyzed.

0.1972 gram salt gave 0.0523 gram Ag.

	Calculated for $C_{18}H_{18}O_3NAg$.	Found.
Ag	26.69	26.52

β-p-Tolylglutaranil.—When the acid just described is heated above its melting-point, water is given off and a slight decomposition takes place. On cooling, the liquid solidifies to a crystalline mass. By recrystallizing from alcohol long, sharp needles are obtained, which melt at 174°.5.

Analysis:

0.2188 gram substance gave 10.7 cc. N at 27°.5 and 730 mm.

	Calculated for $C_{18}H_{17}O_2N$.	Found.
N	5.109	5.164

β-m-NITROPHENYLGLUTARIC ACID.

By S. Avery and M. C. Gere.

While the investigation of the nitrophenylglutaric acids was in progress, Knoevenagel[1] published his synthesis of the meta and para acids. He did not, however, prepare derivatives. Hence our work was continued. We prepared the acid by saponifying in acid solution the tricarboxylic ester formed

[1] Ann. Chem. (Liebig), 303, 235.

by the action of sodium malonic ester on *m*-nitrocinnamic ester.

The tricarboxylic ester was placed in an Erlenmeyer flask and dilute hydrobromic acid added. A quantity of broken glass and scrap platinum was then dropped in to prevent bumping, and the flask placed on a thin piece of asbestos over a wire gauze. It was then connected with the inner tube of a Liebig condenser instead of the ordinary return flow, and heated gently with the flame. After some time a brown, tarry-looking oil settled to the bottom of the flask, but was gradually dissolved. After heating about eight hours the saponification was completed. At the end of the operation most of the acid was in the form of a gray precipitate in the bottom of the flask. As the liquid cooled, more of the acid separated out. The precipitate was filtered off on a Witt plate as a yellowish-gray, amorphous mass. It was then washed with water, and the washings, together with the mother-liquor, evaporated down, and the acid which crystallized out was filtered off. The entire yield was then washed and crystallized from weak alcohol, washed with cold water, and dried in a vacuum.

Part of the acid was purified by converting into the anhydride by means of acetic anhydride, and recrystallizing the resulting anhydride several times, then converting it back into the acid by dissolving in dilute alcohol. The acid thus obtained was distinctly crystalline and almost white. Its melting-point was 205° to 206°. It was found to be easily soluble in alcohol and ether, less soluble in water, very little, if at all, soluble in benzene, chloroform, and petroleum ether.

Analysis:

0.23777 gram acid gave 0.09494 gram H_2O and 0.45628 gram CO_2.

	Calculated for $C_{11}H_{11}O_4N$.	Found.
C	52.17	52.33
H	4.35	4.43

Salts of β-m-Nitrophenylglutaric Acid.

Silver Salt.—White amorphous powder.

Analysis:

0.3329 gram silver salt gave 0.1533 gram Ag.

	Calculated for $C_{11}H_9O_6NAg_2$.	Found.
Ag	46.22	46.05

Calcium Salt.—Calcium chloride produces no precipitate with the ammonium salt of *β-m*-nitrophenylglutaric acid, but on adding alcohol the calcium salt is readily thrown down as a white, flaky precipitate, which is very distinctly crystalline.

Analysis:

0.2005 gram calcium salt gave 0.03615 gram CaO.

	Calculated for $C_{11}H_9O_6NCa.H_2O$.	Found.
Ca	12.916	12.869

Barium Salt.—To a partial solution of the acid in water a solution of barium hydroxide was added from a burette until a faint reaction was given with phenolphthalein. The acid went into solution, but seemed to crystallize out again, so an excess of barium hydroxide was added, and carbon dioxide passed in to precipitate the excess. The solution was then filtered and evaporated on a water-bath. By cooling in a freezing-mixture and constantly stirring, a very finely crystalline, white precipitate separated out. It was filtered, washed, and analyzed.

Analysis:

0.20055 gram barium salt gave 0.1033 gram $BaCO_3$.

	Calculated for $C_{11}H_8O_6NBa$.	Found.
Ba	35.36	35.7

Copper Salt.—Green amorphous powder.

Analysis:

0.20035 gram copper salt gave 0.0402 gram Cu.

	Calculated for $C_{11}H_9O_6NCu$.	Found.
Cu	20.114	20.06

β-m-Nitroglutaric Anhydride.—The anhydride was made by the action of boiling acetic anhydride on the acid. While still hot, a small amount of benzene was added, though not

enough to make two layers. The solution was then filtered and cooled in a freezing-mixture. White, glistening crystals separated out. Upon filtering off and drying, they were found to be very light and silky and, apparently, quite pure, melting sharply at 170°.5. They are insoluble in benzene and petroleum ether, but soluble in alcohol, being changed by it to the acid. They were insoluble in water, which acts on them not at all, or with great difficulty.

Several nitrogen determinations of the anhydride were made, but in each case the amount found was from 0.3 to 0.4 per cent too high. This may be due to the fact that the anhydride contained some impurity which eluded detection, but which evidently did not affect the melting-point, which was quite sharp. However, there is no doubt that the anhydride was obtained, since it yielded *β-m*-nitrophenylglutaranilic acid.

β-m-Nitrophenylglutaranilic Acid.—This acid was made by the action of the anhydride on aniline in benzene solution. It was found that a very pure, white, flaky, crystalline precipitate could be obtained by dissolving the anilic acid in 50 per cent alcohol and then adding petroleum ether until a few white specks appeared in the liquid or until there was a very slight milkiness. Upon standing a short time the precipitate gradually separates out in a very pure condition. The anilic acid melts at 160° C. It is soluble in alcohol, insoluble in petroleum ether and benzene.

	Calculated for $C_{17}H_{16}O_5N_2$.	Found.
N	8.59	8.402

Silver Salt of Anilic Acid.—When made in the usual way by neutralizing with ammonia and precipitating with an excess of silver nitrate, the amount of silver proved to be too large, upon analysis. This was due to the difficulty in washing out the excess of silver nitrate, on account of the extremely gelatinous character of the precipitate formed by the anilic acid; the precipitate closely resembles alumina. It was therefore prepared as follows: Equivalent amounts of silver foil and anilic acid were weighed out. The silver

was converted into silver nitrate and the anilic acid into the ammonium salt by the usual methods. The two solutions, now rather dilute, were mixed together and then heated to boiling. It was then cooled in a freezing-mixture and the gelatinous precipitate formed at once. This was then filtered and washed in the usual way. The salt thus formed was chemically pure, as shown by the analysis.

It is fairly stable when dried below 100°, but when heated to 120° it rapidly becomes black. It is not very readily affected by light.

Analysis:

0.1021 gram silver salt gave 0.0253 gram Ag.

	Calculated for $C_{17}H_{15}O_5N_2Ag$.	Found.
Ag	24.79	24.78

β-*p*-NITROPHENYLGLUTARIC ACID.

By S. Avery and Hal. T. Beans.

Nitration of β-Phenylglutaric Acid.

Twenty-two grams β-phenylglutaric acid, dry and finely pulverized, were gradually added in small portions, to 200 cc. fuming nitric acid, cooled to zero, in a freezing-mixture. The temperature was kept below 10°, remaining between 8° and 10° during the greater portion of the experiment. When all had been added, the reaction-mixture was poured into ice-water, causing a finely-divided, light-yellow precipitate to separate. This was filtered off and washed free from nitric acid with cold water. It was then digested with hot water, filtered, and again digested.

By this treatment two products are obtained. One is practically insoluble in hot water and melts sharply at 237° after recrystallization from dilute alcohol. It was identified as β-paranitrophenylglutaric acid. From 22 grams β-phenylglutaric acid, 18 grams of the pure paranitro acid were obtained, and some later experiments gave even higher yields. The other compound is soluble in hot water and crystallizes out, on standing, in fine, light-yellow crystals, which, after recrystallization from hot water, melt at 175°. This product

has not, as yet, been investigated, but is probably β-orthonitrophenylglutaric acid. Under the conditions of nitration given, the amount of this compound formed does not exceed 10 per cent of the phenylglutaric acid used.

In working with nitric acid of different concentrations it was observed that, as the strength of acid increased and the temperature rose, the amount of water-soluble compound increased. This suggests the similar result obtained in nitrating cinnamic acid, when, with increasing concentration of the nitric acid, the proportion of orthonitrocinnamic acid increases.

To prove that the nitro group occupies the para position, some of the acid was oxidized to the corresponding nitrobenzoic acid by heating with chromic acid in sulphuric acid solution. The resulting product was extracted with ether, in which the nitroglutaric acid is insoluble, while nitrobenzoic acid dissolves. On evaporating the ether a solid was obtained which, after crystallizing from alcohol, melted sharply at 238°. Paranitrobenzoic acid melts at 238°, thus proving the nitroglutaric acid to be a para compound.

β-*p*-Nitrophenylglutaric acid forms almost colorless, hard, short prisms, melting sharply at 237°. It is soluble in alcohol, ethyl acetate, and glacial acetic acid, very difficultly soluble in hot water and benzene, and insoluble in chloroform, ether, and ligroin.

Salts of β-p-Nitrophenylglutaric Acid.

The *silver salt* was made in the usual way. It forms a nearly white, curdy precipitate which, when dry, is very stable in the light.

Analysis:

0.6190 gram salt gave 0.2853 gram Ag.

	Calculated for $C_{11}H_9NO_6Ag_2$.	Found.
Ag	46.22	46.09

The *calcium salt* was made by neutralizing the acid with calcium hydroxide at boiling temperature. The solution was concentrated and alcohol added, when the salt precipitated

out in white, glistening flakes. The salt is soluble in water but insoluble in alcohol.

Analysis:

After drying the salt at 100°, the calcium was determined by igniting and weighing as the oxide.

0.2061 gram salt gave 0.0387 gram CaO.

	Calculated for $C_{11}H_9NO_6Ca$.	Found.
Ca	13.74	13.41

The salt may have retained some water.

The *barium salt* was prepared in a similar way. It separates as a white, silky, crystalline precipitate and is somewhat less soluble than the calcium salt.

Analysis:

The barium was determined by igniting and weighing as the carbonate.

0.1530 gram salt gave 0.0780 gram barium carbonate.

	Calculated for $C_{11}H_9NO_6Ba$.	Found.
Ba	35.36	35.46

β-p-Nitrophenylglutaric anhydride is formed by dissolving the acid in boiling acetic anhydride and then adding dry benzene. On cooling, it separates in fine, light-yellow crystals. After recrystallization from acetic ether it forms clear crystals of slightly yellowish color, melting at 122°.5. It is comparatively stable, water acting on it with difficulty. It is soluble in acetic ether, difficultly soluble in hot benzene, and insoluble in cold benzene. It dissolves in hot, dilute alcohol, being converted back into the acid which separates, on cooling, in almost colorless, glistening crystals, melting at 237°.

Analysis:

0.1093 gram anhydride gave 0.2265 gram CO_2 and 0.0390 gram H_2O.

0.2447 gram anhydride gave 13.9 cc. N at 26° and 728 mm.

	Calculated for $C_{11}H_9NO_5$.	Found.
C	56.14	56.51
H	3.87	3.98
N	5.95	6.02

β-p-Nitrophenylglutaric Dimethyl Ester.—The dimethyl ester was prepared by treating the anhydride in absolute methyl alcohol, with dry gaseous hydrochloric acid. After saturation with hydrochloric acid, the excess of alcohol was evaporated off on the water-bath and the residue cooled and stirred, when it solidified into a crystal mass. This was washed with water, dried, and recrystallized from ethyl alcohol. The ester forms large, almost colorless, plates, which melt very sharply at 62°. It is insoluble in water but very soluble in alcohol.

Analysis:

I. 0.2033 gram ester gave 9.6 cc. N at 21° and 729.8 mm.

II. 0.2664 gram ester gave 12.7 cc. N at 24° and 734.7 mm.

	Calculated for $C_{13}H_{15}NO_6$.	Found. I.	Found. II.
N	4.98	5.18	5.14

β-p-Nitrophenylglutaranilic Acid.—One gram *β-p*-nitrophenylglutaric anhydride was dissolved in about 15 cc. of hot, dry benzene with the addition of a little alcohol-free acetic ether. To the hot solution was added 0.416 gram freshly distilled aniline dissolved in a little benzene, and the mixture brought to boiling. On cooling, needle crystals of slightly yellow color separated out. These melt at 105° with the liberation of the vapor of benzene. After crystallizing from dilute alcohol, the crystals are light, glistening flakes, melting at 120° to 121°. The melting-point is not further changed by crystallizing from ethyl acetate. It must be noted here that the melting-point is not constant unless the heat is very carefully applied, since the substance very readily loses water to form the anil.

Silver Salt of the Anilic Acid.—The silver salt is a white, gelatinous precipitate. It is stable when heated to 120° and does not readily blacken in the light.

Analysis:

0.1336 gram salt gave 0.0332 gram Ag.

	Calculated for $C_{17}H_{18}N_2O_5Ag$.	Found.
Ag	24.79	24.85

β-p-Nitrophenylglutaranil.—On heating the anilic acid in a crucible supported inside a larger crucible, it first melts and then gives off water vapor, forming a clear, brownish liquid. Toward the end of the reaction there is a slight further decomposition, as shown by the liberation of a heavy vapor having the odor of burning nitrogenous matter. At this point the heating is stopped and the contents of the crucible allowed to cool. There is obtained a clear, brittle glass, soluble in acetone and glacial acetic acid. From either of these solvents the anil crystallizes in fine, white needles, which melt at 203°.

THE ACTION OF FUSED SODIUM DIOXIDE ON METALS.

[SECOND PAPER.[1]]

BY WM. L. DUDLEY.

1. Nickelo-Nickelic Oxide, Ni_3O_4.—On heating nickelo-nickelic hydrate (prepared by fusing sodium dioxide in a nickel crucible) to 240° C., a black, lusterless, amorphous powder remains, consisting of nickelo-nickelic oxide, Ni_3O_4. It is hygroscopic and absorbs 7.4 per cent of water from the air at 30° C., but it loses it completely at 110° C. It dissolves in hydrochloric acid with the evolution of chlorine, in sulphuric and nitric acids with the evolution of oxygen. It is non-magnetic.

Daubigny[2] describes a gray, non-magnetic solid, of metallic appearance, obtained by passing oxygen over $NiCl_2$ at 350° to 440° C., as Ni_3O_4, but he gives no results of analysis, and his description does not accord with that of Ni_3O_4, prepared by heating $Ni_3O_4,2H_2O$, as described above.

2. Magnetic Ferric Hydrate, Fe_2O_3,H_2O.[3]—Iron is very

[1] The publication which the author considers the "first paper" under the above title appeared in the *Journal of the American Chemical Society*, 18, 901, with the caption "Nickelo-Nickelic Hydrate, $Ni_3O_4,2H_2O$."

[2] Compt. rend., 87, 1082.

[3] A paper, describing the action of fused sodium dioxide on iron, was read by the author before the Chemical Section at the Boston meeting of the A. A. A. S., in 1898, but it was not then presented for publication, since the investigation was incomplete.

rapidly attacked by fused sodium dioxide, especially if it be heated to bright redness. An ordinary sheet-iron crucible will rarely withstand more than one or two fusions without perforation. Clippings of iron put into the crucible will protect it to some extent and at the same time hasten the action of the sodium dioxide.

If the fusion is kept at a bright-red heat for thirty minutes the action will usually be complete, but at dull redness some of the sodium dioxide will remain undecomposed for three and a half hours, or longer.

On treating the fused mass with water, a crystalline iron compound remains undissolved. If manganese be present in the iron the solution will have a purple color, due to the presence of sodium permanganate produced by the oxidizing action of the sodium dioxide, provided the temperature of bright redness has been employed in making the fusion; but if it be made at a very high red heat the solution will be colorless, owing to the decomposition of the sodium permanganate, while at a dull red heat sodium manganate will be formed and the solution will consequently have a green color.

The iron compound consists of tabular, scale-like crystals, with outlines too indefinite for an accurate determination of their form. The color varies from reddish-brown to rich garnet. When the crystals are larger they are dark-red, frequently appearing to be black. The streak is brown. The specific gravity is 3.8 at 27° C.

The crystals are decidedly magnetic. When heated to redness they sinter together, but the residue is still magnetic.

The compound, prepared as described above, was freed from alkali by washing first by decantation and then in a Soxhlet apparatus until no alkalinity could be detected by means of phenolphthalein in the washings. This result was usually attained in about fifty hours. The compound was then dried over calcium chloride, since there was found to be a slight loss of water at 100° C.

Analysis of the compound proved that the formula was Fe_2O_3,H_2O, as shown below:

	Calculated for Fe_2O_3,H_2O.	Found. I.	II.
Fe	62.92	62.86	62.96
H_2O	10.11	9.94	10.09

The presence of ferrous oxide could not be detected.

After heating the crystals to low redness the residue, though magnetic, proved to consist of Fe_2O_3, as shown by the following analysis:

	Calculated for Fe_2O_3.	Found.
Fe	70.00	70.03

Several authors[1] have described the preparation of Fe_2O_3, H_2O by various methods, involving the use of the alkalies, fused or in solution, but its properties, as described by them, differ very materially from those of the compound made by fused sodium dioxide.

The crystalline hydroxide is formed during the fusion with the sodium dioxide and not by the decomposition of sodium ferrite (Fe_2O_3,Na_2O) when water is added. If sodium ferrite is formed during the fusion it is decomposed as the temperature rises and the crystals of Fe_2O_3,H_2O are formed in the crucible. On treating the fused mass with water the crystals remain intact. The formation of the hydroxide in the fusion is accounted for by the presence of sodium hydroxide, which usually varies from 8 to 25 per cent in all samples of sodium dioxide. The reaction may be represented as follows:

$$2Fe + 3Na_2O_2 + 2NaOH = Fe_2O_3,H_2O + 4Na_2O.$$

I am indebted to Mr. W. P. Connell for the analytical work done in the investigation of this compound.

3. Gold.—Fused sodium dioxide attacks gold very rapidly and leaves it in a spongy state. The gold seems to be oxidized, but the oxide formed decomposes at the temperature of fusion of the sodium dioxide and does not re-form on cooling, therefore the gold remains in the form of sponge.

Au_2O_3 gives off some oxygen at 110° C., and at 160° C. AuO

[1] Muck: Ztschr. Chem., [2], 4, 41; P. de Saint Gilles: Ann. chim. phys., [3], 46, 47; Brunck and Graebe: Ber. d. chem. Ges., 13, 725; Schiff: Centrbl., I., 1860, p. 1768; Rousseau and Bernheim: Compt. rend., 106, 1530; Rousseau: Compt. rend., 110, 1032; van Bemmelen and Klobbie: J. prakt. Chem., 46, 497-529.

remains, which, in turn, is decomposed at 250° C., leaving metallic gold.

4. Silver.—When sodium dioxide is fused in a silver crucible the metal is so rapidly attacked that a vessel of ordinary thickness will be perforated after three or four fusions, even if scraps of silver be added. When the fusion is conducted at full red heat, the action ceases in from twenty to thirty minutes, and the fused mass will be filled with needle-shaped crystals. On treatment with water the silver compound remains, for the most part, undissolved, although the alkaline solution will contain some silver.

An endeavor was made to wash the compound in a Soxhlet extractor, but it was found that the glass of the apparatus was slowly attacked and that the silver compound slowly dissolved. The washings gradually became wine-colored and dichroic, and finally a black precipitate separated. The washings maintained decided alkalinity. In order to determine the result of continued washing, this process was carried on daily for about three months, at the end of which time the washings were still alkaline and wine-colored, although the dichroic effect had gradually diminished. The residue in the thimble was comparatively small and quite black. The glass of the extractor was decidedly attacked and deeply stained.

The precipitate which separated from the washings was black and amorphous. It was readily attacked by nitric acid, which dissolved it, leaving a small quantity of white residue. Analysis gave it the following composition:[1]

Ag_2O	84.25
Na_2O	2.67
SiO_2	13.22

[1] It cannot be asserted that this is a definite silicate, since the existence of silver silicate is uncertain. The analysis, however, indicates that it may be a complex double silicate having the formula $17Ag_2O,2Na_2O,10SiO_2$ ($Ag_{34}Na_4Si_{10}O_{39}$), which would have the following percentage composition:

Ag_2O	84.44
Na_2O	2.67
SiO_2	12.89

The compound sustained the following losses on heating:

105° C.	1.00
250° C.	2.78
Redness	5.52

This loss was oxygen, doubtless from the Ag_2O in the compound, and should be 5.84 per cent, if all of the silver oxide it contained were thus reduced.

The wine-colored solution from the extractor was found to contain 1 part of solid matter in 2777 parts of water, at 20° C. On evaporating to dryness a black, scaly residue remained, 58.24 per cent of which could be redissolved in water. It was partly soluble in acids. The residue was found to contain:

Ag	20.66
SiO_2	29.07
Na_2O	21.93

together with various impurities from the eroded glass.

The plan of washing out the alkali from the silver compound had to be abandoned and the following method was adopted: After dissolving the fusion-product in water, the solution was decanted from the crystalline silver compound, more distilled water was poured over it, and a drop or two of phenolphthalein was added as an indicator. The excess of alkali was then carefully neutralized with acetic acid, the silver compound filtered out and washed with cold distilled water. It was found that filter-paper was attacked by the compound, and, therefore, a Gooch crucible of platinum, with platinum sponge as the filtering medium, was employed.

The crystals possess a gray and somewhat metallic luster. They are, apparently, flattened and elongated prisms, some of them showing oblique termination and suggesting monoclinic symmetry.

The compound was dried in a desiccator over calcium chloride, and on analysis was found to contain:

Ag	97.99
O	1.82

Assuming the crystals to be a mixture of silver oxide and metallic silver, the proportion would be:

Ag_2O	26.31
Ag	73.69

But 1.8245 per cent, which was the actual amount of oxygen found in the crystals, corresponds so closely to the theoretical proportion of oxygen which there would be in Ag_8O—*i. e.*, 1.825 per cent, that further investigation was made to determine this point. The crystals were digested with strong ammonium hydroxide (which readily dissolves Ag_2O) for twenty-four hours, filtered, washed, and dried over calcium chloride. On analysis the substance was then found to contain only 0.175 per cent of oxygen, showing that about nine-tenths of the silver oxide had been dissolved and that the crystals probably consist of a mixture of silver oxide (Ag_2O) and silver; or, that if the oxide Ag_8O (which has never been described) does exist, it is decomposed by ammonium hydroxide into silver oxide and silver, which is not probable.

I am indebted to Mr. C. B. Farrington for the analyses of the silver residues from the Soxhlet extractor.

5. Platinum Sesquioxide (Pt_2O_3) *and Hydroxide* (Pt_2O_3, $2H_2O$).—Platinum is rapidly attacked by fused sodium dioxide. In a spongy or finely-divided state and intimately mixed with sodium dioxide, platinum burns almost like tinder when heated to redness. If the combustion be started in a portion of the mixture it is transmitted rapidly throughout the mass, which becomes heated to bright redness. A platinum crucible withstands very few fusions of sodium dioxide.

Platinum sponge was fused with sodium dioxide in a platinum capsule until the mass became tranquil. The fusion-product was treated with water and a platinum compound of yellowish or muddy-green color remained undissolved. It settled slowly and was so finely divided as to render filtering impossible. It was washed several times by decantation and the remaining alkali was carefully neutralized with acetic acid. When neutral, the compound became yellow or very light brownish-yellow, resembling precipitated stannic sulphide in color. When the alkali was neutralized with carbon dioxide, or even when the compound was simply washed with distilled water until all of the alkali was removed, the same

color change was produced. The yellowish-green compound is doubtless a very unstable sodium salt of the yellow hydroxide which is obtained on neutralizing, or on washing out, the alkali. Therefore the hydroxide has slightly acid properties.

The compound, after neutralizing the alkali, was washed by decantation until nearly pure, since it was not practicable to filter it, owing to its fine state of division. It was then dried over calcium chloride, thrown on a filter, washed a few times with dilute sulphuric acid, and finally with distilled water. Thus the alkali was all removed and the mass was again dried over calcium chloride.

Analysis proved the compound to have the formula Pt_2O_3, $2H_2O$, as shown below:

	Calculated for $Pt_2O_3,2H_2O$.	Found. I.	II.
Pt	82.23	82.21	81.99
O	10.15	10.20	10.36
H_2O	7.62	7.59	7.65

The water was determined by direct weighing in a calcium chloride tube, the platinum by weighing the residue after heating to redness, and the oxygen by difference. The following reactions may represent the formation of the hydroxide:

$$2Pt + 3Na_2O_2 = Pt_2O_3,2Na_2O + Na_2O;$$

$$Pt_2O_3,2Na_2O + 4HC_2H_3O_2 = Pt_2O_3,2H_2O + 4NaC_2H_3O_2;$$

or $Pt_2O_3,2Na_2O + 4H_2O = Pt_2O_3,2H_2O + 4NaOH$.

$Pt_2O_3,2H_2O$ is insoluble in alkalies, but it is reduced to platinum black on boiling with sodium hydroxide and alcohol. With acid the reduction does not take place. It is insoluble in nitric and sulphuric acids, also in cold dilute hydrochloric acid. Hot concentrated hydrochloric acid dissolves it slowly in the presence of air, forming platinic chloride. It dissolves slowly in aqua regia. The other hydroxides of platinum are readily soluble in acids. It is apparently unchanged on fusing with sodium hydroxide. It is reduced to platinum with incandescence on warming slightly in a current of hydrogen or coal gas. It does not lose water

at 100° C., but at 385° it loses 5.22 per cent, and at about 450° it is changed to Pt_3O_3. On heating to redness it is reduced to metallic platinum.

Platinum sesquioxide is a dark-brown, amorphous powder. It is insoluble in nitric, sulphuric, and hydrochloric acids, but dissolves slowly in concentrated hydrochloric acid in contact with air, forming platinic chloride. No salts corresponding to this oxide have been obtained.

The isolation of platinum sesquioxide fills a gap in the list of oxides of platinum which brings it into conformity with the other metals of this group, since osmium sesquioxide and iridium sesquioxide have long been known, as well as the sesquioxides of ruthenium and rhodium, palladium now being the only metal in the eighth group which has had no sesquioxides described. The corresponding sulphide of platinum, Pt_2S_3, has been described by Schneider.[1]

VANDERBILT UNIVERSITY,
May 15, 1902.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XXXVIII.—ON THE SPECIFIC HEATS AND HEAT OF VAPORIZATION OF THE PARAFFIN AND METHYLENE HYDROCARBONS.

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Since 1819, when Dulong and Petit, on the basis of their work on thirteen of the chemical elements, announced the law that atoms of all elementary bodies possess the same capacity for heat, or that the specific heats of the elements vary inversely as their atomic weights, the specific heats of the elements have been important physical constants. With some exceptions, the constant 6.54 represents the product of the atomic weight into the specific heat. Later work showed that this law could be extended to compounds. In 1831, Neumann discovered that compounds with analogous composition have the same specific heat. Or in a series of compounds with analogous composition the specific heat varies inversely as the molecular weight. These laws apply to approximately 40 elements, and to solids only much below

[1] Pogg. Ann., 136, 105.

their melting-points. The specific heats of many organic compounds have since been determined, and although no law has been stated, it is evident that, in certain homologous series of organic compounds, a condition exists in some of these series analogous to the law of Neumann. For instance, determinations have been made on a few of the alcohols with the following results:

Ethyl alcohol	0.680
Isopropyl alcohol	0.5286
Isobutyl "	0.5078
Isoamyl "	0.4932

That the variations on certain homologous series, so far as they have been observed, do not conform to a general law is shown by the following series, in which the specific heats increase with increase in molecular weights:

Methyl dichloracetate	0.3202
Ethyl dichloracetate	0.3384
Propyl dichloracetate	0.3506

In general, the data on specific heats of organic compounds are meager and not concordant. For the same substance the results of different observers seldom agree in the third decimal place; they often do not agree in the second, and even in the first place (see tables of Landolt and Börnstein). These variations are probably due to the fact that specific heat is materially affected by impurities in the substance and the temperatures at which it is taken. Then, furthermore, the details of the determinations demand very careful attention to insure concordant results. In the determinations of the hydrocarbons to be described in this paper, it was found that impurities depressed the specific heats very considerably.

Although the paraffin series of hydrocarbons offers the best field for study of an homologous series, very little has been done in the direction of ascertaining the specific heats of these bodies. In a study of distillates separated from Pennsylvania petroleum, by Bartoli and Stracciati,[1] the specific heats of the following hydrocarbons were determined:

[1] Gazz. chim. ital., 15, 417.

Hexane	C_6H_{14}	0.5042	16°–37°
Heptane	C_7H_{16}	0.4869	16°–37°
Octane	C_8H_{18}	0.5111	12°–19°
Decane	$C_{10}H_{22}$	0.5057	14°–18°
Tetradecane	$C_{14}H_{30}$	0.4995	
Hexadecane	$C_{16}H_{34}$	0.4963	15°–22°

The inference derived from these results was that the specific heats of these hydrocarbons were remarkably constant.

No data could be found relating to the specific heats of the methylene hydrocarbons C_nH_{2n}, nor those of the series still poorer in hydrogen. With the greatly extended uses of crude petroleum and refined distillates for fuel, in gasoline and oil engines, accurate information concerning specific heat and heat of vaporization is greatly desired.

Having in hand a great variety of hydrocarbons of the various series, which have been prepared in as pure form as possible, and numerous inquiries having been received for more complete information concerning these physical properties, it seemed advisable to make some determinations of these constants.

The hydrocarbons of the series C_nH_{2n+2} were obtained from Pennsylvania petroleum, those of the other series from California petroleum. Each hydrocarbon had been separated by a long process of distillation, and purified by treatment with sulphuric acid, sodium hydrate, and drying over sodium.

The determinations were made in a Bunsen ice calorimeter, to which was attached a capillary side-tube 70 cm. long, and the bore of such size that 1 cm. contained 0.0579 gram of mercury. To maintain the temperature at 0° the calorimeter was placed in a jar of ice-water with an excess of ice, and this jar was placed in another jar and the space between filled with cotton. The calorimeter was filled with air-free water and dry mercury, and the inside film of ice, 2 to 3 mm. thick, was formed by evaporation of ether by an air-blast within the inner tube. Approximately 2 grams of the hydrocarbon were placed in a small glass-stoppered tube of thin glass, whose heat equivalent was determined. The tube and hydrocarbon were heated to 50° in a larger tube placed in a beaker of water, kept at this temperature for at least fifteen minutes,

then transferred by a thread to the calorimeter. With care this could be done without loss of heat by radiation. The contraction of the mercury column was from 15 to 25 cm.

This method can be used for the paraffin hydrocarbons from C_6H_{14} to $C_{16}H_{34}$, the limit at which the hydrocarbons remain wholly liquid at 0°.

After obtaining the water constant of the apparatus, three to six determinations of each hydrocarbon were made at the temperatures 0° and 50°, with results given in the following table :

	Boiling-points.	Specific heat.
C_6H_{14}	68°	0.5272
C_7H_{16}	91°	0.5005
C_7H_{16}	98°	0.5074
C_8H_{18}	125°	0.5052
C_9H_{20}	151°	0.5034
$C_{10}H_{22}$	162°	0.4951
$C_{10}H_{22}$	172°	0.5021
$C_{11}H_{24}$	195°	0.5013
$C_{12}H_{26}$	214°	0.4997
$C_{13}H_{28}$	226°	0.4986
$C_{14}H_{30}$	242°	0.4973
$C_{15}H_{32}$	260°	0.4966
$C_{16}H_{34}$	275°	0.4957
Commercial gasoline		0.5135
Crude Ohio petroleum		0.4951

The following table gives the specific heats obtained from the series of methylene hydrocarbons :

	Boiling-points.	Specific heat.
C_6H_{12}	68°	0.5062
C_7H_{14}	98°	0.4879
C_8H_{16}	119°	0.4863
C_9H_{18}	135°	0.4851
$C_{10}H_{20}$	160°	0.4692
$C_{11}H_{22}$	190°	0.4819
$C_{12}H_{24}$	212°	0.4570
$C_{13}H_{26}$	232°	0.4573
$C_{14}H_{28}$	244°	0.4531
$C_{15}H_{30}$	263°	0.4708

It appears from these results that there is a uniform decrease in specific heat with increase in molecular weight. Furthermore, the normal hydrocarbons, such as heptane,

C_7H_{16} (b. p. 98°), and decane, $C_{10}H_{22}$ (b. p. 172°), have higher specific heats than their isomers, such, for example, as isoheptane, C_7H_{16} (b. p. 91°), and isodecane, $C_{10}H_{22}$ (b. p. 162°).

The same variation also appears in the methylene series, with high values for certain members that probably indicate different structural relations.

It is further interesting to observe the materially lower values given by the methylene hydrocarbons as compared with the values for the paraffin hydrocarbons. Whether this be due to greater compactness in the methylene molecule or to some quality of its ring structure, it would be interesting to ascertain.

Perhaps the falling off in specific heat with increasing molecular weight will appear to better advantage when arranged as ordinates on a curve with the molecular weights as abscissae. Only those compounds are given on the curve that are known to be normal, although, of course, this is not known with reference to the higher members. The different values of the isomers heptane and decane are shown on the shorter curve.

This uniform decrease in specific heat with increasing molecular weight in the series C_nH_{2n+2} suggests a constant relation analogous to the law of Neumann.

If the constant K be expressed in terms of the specific heat multiplied by the molecular weight and the product divided by the number of atoms in the molecule, the specific heats found for the hydrocarbons of this series give the following values for the constant:

Hydrocarbon.	Molecular weight.	Specific heat.	No. of atoms.	K.
C_6H_{14}	86	0.5272	20	2.26
C_7H_{16}	100	0.5074	23	2.21
C_8H_{18}	114	0.5052	26	2.21
C_9H_{20}	128	0.5034	29	2.22
$C_{10}H_{22}$	142	0.5021	32	2.23
$C_{11}H_{24}$	156	0.5013	35	2.23
$C_{12}H_{26}$	170	0.4997	38	2.23
$C_{13}H_{28}$	184	0.4986	41	2.24
$C_{14}H_{30}$	196	0.4973	44	2.23
$C_{15}H_{32}$	210	0.4966	47	2.24
$C_{16}H_{34}$	224	0.4957	50	2.23

The constant, therefore, for the homologous series of hydrocarbons C_nH_{2n+2} is 2.23.

A similar curve drawn for the specific heats of the methylene hydrocarbons, so far as they were determined, show also a regular variation.

The constant K, for the methylene hydrocarbons, calculated from the determinations, shows a somewhat higher mean value than that of the paraffin hydrocarbons :

Hydrocarbon.	Molecular weight.	Specific heat.	No. of atoms.	K.
C_6H_{12}	84	0.5062	18	2.26
C_7H_{14}	98	0.4879	21	2.28
C_8H_{16}	112	0.4863	24	2.37
C_9H_{18}	126	0.4851	27	2.27
$C_{11}H_{22}$	154	0.4819	33	2.25
$C_{15}H_{30}$	210	0.4708	45	2.20

The values for the specific heats of both hexane and hexamethylene are higher than should be expected from the results on the other members of the series. These hydrocarbons were well purified, except it seems probable that the distillates contained certain proportions of both.

Determinations were also made of the specific heats of a series of hydrocarbons separated from the high-boiling portions of Pennsylvania petroleum. This series is under examination to establish its composition and relations to series separated from heavy petroleums from other fields. These hydrocarbons were cooled to —10°, and filtered to remove so far as possible the solid hydrocarbons with which they are associated in Pennsylvania petroleum. They have been shown to be members of the series C_nH_{2n}. A more detailed description of these bodies will be presented in a subsequent paper, which is now in preparation.

The following values were obtained for the specific heats of these hydrocarbons :

	Boiling-point.	Specific heat.
$C_{16}H_{32}$	173°	0.4723
$C_{18}H_{36}$	202°	0.4723
$C_{20}H_{40}$	223°	0.4706
$C_{23}H_{46}$	260°	0.4612
$C_{24}H_{48}$	272°	0.4586

From data obtained with the paraffin hydrocarbons, there is no opportunity to compare the specific heats, although the sudden drop from the last member examined of the series C_nH_{2n+2}, $C_{16}H_{34}$ (specific heat 0.4957), to the first member of the last series above in which the solid hydrocarbon, $C_{18}H_{32}$ (specific heat 0.4723), had been removed by cooling and filtration, shows a marked difference in structure. This relation appears in the longer curve in the table.

Comparing the last member of the series C_nH_{2n} from California oil $C_{15}H_{30}$ (specific heat 0.4708), with the hydrocarbon $C_{16}H_{32}$ (specific heat 0.4746), it appears that the series C_nH_{2n} from Pennsylvania petroleum is a continuation of the same series from California petroleum. Unfortunately, the higher members of the series from California petroleum were not available for comparison. But results already obtained as to the composition, specific gravity, refractive index, etc., are in accord with the specific heats. The specific heat was also determined in several hydrocarbons of the series C_nH_{2n-2}, and the series C_nH_{2n-4}, which had been separated from Texas petroleum with the following results:

Series C_nH_{2n-2}.

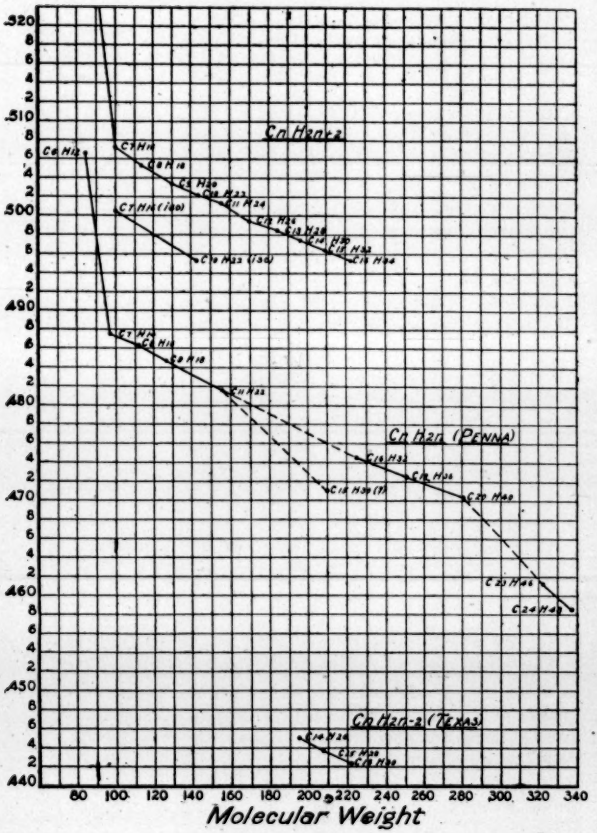
	Boiling-point at 50 mm.	Specific heat.	K.
$C_{14}H_{26}$	127°	0.4447	2.15
$C_{15}H_{28}$	142°	0.4439	2.15
$C_{16}H_{30}$	162°	0.4426	2.14

Series C_nH_{2n-4}.

	Boiling-point at 50 mm.	Specific heat.
$C_{21}H_{38}$	218°	0.4560
$C_{25}H_{46}$	273°	0.4650

The latter results cannot be accepted as reliable, for the quantities of the hydrocarbons were very small, and the oils began to crystallize at 0°. There is no doubt that the specific heats of these hydrocarbons are smaller than those of the preceding series.

To convey a clear idea of the variation in hydrocarbons in the same series, and also to show the difference between the different series, the results are brought together on the following coordinate table:


CnH2n+2
CnH2n (PENNA)
CnH2n-2 (TEXAS)
Molecular Weight

The regular variation in members of the series C_nH_{2n+2} appears in its curve, and the differences in what are known to be isomeric forms in the same series. It is further interesting to observe the continuation of the curve representing the members of the series C_nH_{2n} from the curve containing the members of the series C_nH_{2n} from California petroleum. The lower values in the series C_nH_{2n-2} from Texas petroleum form a characteristic curve near the base of the table.

The specific heat was determined in the following crude oils from various fields :

	Specific gravity.	Specific heat.
Pennsylvania	0.8095	0.5000
Berea grit	0.7939	0.4690
Japanese	0.8622	0.4532
Texas (Lucas well)	0.9200	0.4315
Russian	0.9079	0.4355
Wyoming	0.8816	0.4323
California	0.9600	0.3980
Texas	0.9466	0.4009
Ohio	....	0.4951
Commercial gasoline	....	0.5135

These values show that the specific heat of the crude oils is an important property from a practical point of view. It also appears that there is no close agreement between specific heat and specific gravity. Pennsylvania oil stands at the head, and Berea grit, with a much larger proportion of volatile constituents, is next. Of the heavier oils, it appears in general that the specific heats are much lower, but with no definite relation.

It would be interesting to ascertain the specific heats of the less volatile constituents of petroleum from different fields, including the solid hydrocarbons. This would require observations at different temperatures, and it would add to the interest of the data if all determinations could be made within a wide range of temperatures.

Heats of Vaporization of Hydrocarbons of the Paraffin and Methylene Series.

Since it had been found that a boiling-point constant can be calculated from the absolute boiling-point and latent heat of

evaporation, which may be used as a basis of a method for the determination of molecular weights, more complete knowledge of the latent heat of evaporation or heat of vaporization of liquids at their boiling-points has become of great importance. From a practical point of view, the greatly extended use of crude petroleum and its constituents can only be economically continued with the aid of further information concerning the heats of vaporization. Numerous inquiries from persons interested in these directions attest an appreciation of further knowledge on this subject.

In 1885 the following law was proposed by Dudley, on the heats of vaporization of members of a homologous series.[1]

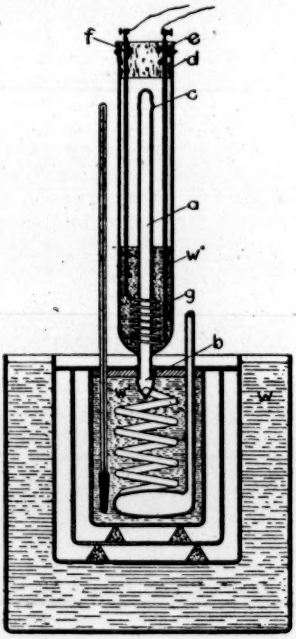
"In any homologous series the heat of vaporization in a unit of volume of the vapor, under the same conditions of temperature and pressure, is proportional to the density and also to the absolute boiling-point." This generalization was based on data selected from determinations of the heats of vaporization of the formates, acetates, propionates, butyrates, isobutyrates, alcohols, and aromatic hydrocarbons.

With numerous members of the different series of hydrocarbons at hand, it was our intention to determine the latent heats of the series C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-2}. But the only apparatus available was constructed of glass, which would not withstand the high temperatures necessary in determinations of the hydrocarbons with high boiling-points, and the time was too limited to permit of the construction of a metallic apparatus.

For the apparatus used we are indebted to the kindness of Professor Kahlenberg, of the University of Wisconsin, who allowed us to use the form devised by him, before he had published his description, which appeared in the *Journal of Physical Chemistry*, **5**, 215 (1901).

This apparatus is an ingenious modification of Berthelot's method, in which the substance is heated and volatilized by means of an electric current within the body of the liquid, thus avoiding errors due to external heating. Through the kindness of Professor Kahlenberg and Professor Trevor we

[1] J. Am. Chem. Soc., 17, 985.



are able to show, in this connection, the form of this apparatus.

In the publication referred to, the apparatus is described as follows: "The retort consists of a tube 17 cm. long and 5.5 cm. in diameter, into the bottom of which is fused a tube which fits into a condenser with a ground-glass joint. At the other end of the inner tube are two large lateral openings. Glass tubes pass through the cork at the top, and into these are fused the ends of the spiral of platinum wire. This spiral consists of about 40 cm. of fairly stout platinum wire, to the ends of which are welded short, heavy pieces of platinum rod,

and these rods are, in turn, fused into the glass tubes. Long, rather heavy copper wires pass down into the glass tubes, at the bottom of which they are connected with the ends of the platinum rods by means of a few drops of mercury. The calorimeter is covered with a heavy piece of asbestos board and the retort is enclosed in asbestos and cotton batting."

A current of from 8 to 10 amperes, regulated by a rheostat, gave sufficient heat to vaporize from 20 to 30 grams of the oil in from five to six minutes. The calorimeter, about 2500 cc. capacity, was made of thin nickel-plated sheet copper. It was elliptical in form, to conform to the shape of the condenser, and was provided with a copper stirrer. The capacity of the calorimeter was reduced, as shown in the figure, by bending closer together the glass tubes leading from the body of the condenser. Temperatures were taken on a Beckmann thermometer.

The water equivalent of the calorimeter, condenser, stirrer, and thermometer were found to be 185 grams, practically the same value as the equivalent calculated from the weights and specific heats of the parts of the apparatus.

As mentioned above, this form of the apparatus is limited in this work by the fact that when oils of boiling-points higher than 125° are volatilized, the sudden change in temperature at the water line of the condenser is so great that glass will not stand it.

The following results were obtained with a few members of the series C_nH_{2n+2}, as the mean of several observations :

	Boiling-point.	Heat of vaporization in calories.
Hexane, C_6H_{14}	68°	79.4
Heptane, C_7H_{16}	98°	74.0
Octane, C_8H_{18}	125°	71.1

Determinations were also made on the methylene hydrocarbons that could be volatilized in this form of apparatus :

	Boiling-point.	Heat in calories.
Hexamethylene, C_6H_{12}	68°–70°	87.3
Dimethylpentamethylene, C_7H_{14}	90°–92°	81.0
Methylhexamethylene, C_7H_{14}	98°	75.7
Dimethylhexamethylene, C_8H_{16}	118°–119°	71.7

These results indicate a rapid falling off in latent heat, with increase in molecular weight. It is to be regretted that we had not the metallic condenser, which would have enabled us to carry these observations up to include the less volatile hydrocarbons of both series. Advantage will be taken of the earliest opportunity to continue this work.

The hydrocarbons used in the work described in this paper were prepared with assistance granted by the Academy from the C. M. Warren Fund for Chemical Research.

REPORT.

Algal Wax and Its Relationship to Petroleum.

It will be remembered that Kraemer and Spilker[1] published a new theory of the formation of petroleum, which assumed that the oil contained in diatoms was probably the raw material from which mineral wax, petroleum, and natural gas were derived by natural distillation. They obtained a considerable quantity of a recent diatomaceous deposit from which a wax-like substance was extracted by means of benzene. This, by distillation under pressure, yielded a liquid resembling crude petroleum, besides gaseous products, and a residue consisting of carbon and paraffin.

Engler,[2] in his reply to this article, calls attention to one by Stahl[3] which was not mentioned by Kraemer and Spilker. Stahl suggested essentially the same idea, except that he believed the deposits to have been formed in more or less enclosed arms of former seas, instead of in fresh-water lakes. Engler then calls attention to his own well-known suggestion that petroleum is derived from deposits of marine animals. The fat contained in them is first saponified by water, and finally changed to petroleum by pressure and heat, or possibly by pressure alone. Zaloziecki and others regarded mineral wax as an intermediate product, but Engler thinks the evidence is not sufficient to warrant such a conclusion. It is well known that mineral wax was distilled on a large scale to obtain petroleum and paraffin.

By the distillation of stearic and oleic acids and their glycerides, and of fish oil, Engler[4] obtained petroleum, and he showed later[5] that "all possible kinds of animal and vegeta-

[1] Ber. d. chem. Ges., **32**, 2940 (1899); see also this JOURNAL, **23**, 176.
[2] *Ibid.*, **33**, 7 (1900).
[3] Chem. Ztg., (1889), p. 144.
[4] Ber. d. chem. Ges., **21**, 1716; **22**, 592.
[5] *Ibid.*, **30**, 2358.

ble fats and oils" could be changed to petroleum. Hence it would have been surprising if Kraemer and Spilker had not obtained petroleum by distilling diatom fat, mineral wax, and Carnauba and Japan waxes. As all vegetable and animal fats yield practically the same products when distilled under pressure, this evidence is of no value in deciding between the two theories.

The comparison of the composition of the ash of the diatomaceous deposit and that of the oil-bearing rock is of no value, because, as Kraemer and Spilker acknowledge, the diatoms must have been buried under detritus from the surrounding hills. Even a closer agreement in their composition would have been of no value in deciding the question under discussion.

Kraemer and Spilker thought that the chief objection to Engler's theory was that it was not easy to account for the vast deposits of marine animals necessary to form the petroleum. Engler replied that by alternate rising and sinking of the shore, bays might be cut off from the sea and develop new fauna as the water became less salt. These animals would be killed when the shore sank and the salt water was readmitted. Deposits of animal remains might also be formed by fresh water killing marine species, or by the over-production of animal life owing to the lack of carnivora. Also diseases, or earthquakes, or submarine volcanic activity may be mentioned. But above all is the action of currents that carry animal remains into bays or other sheltered places. It is probable that the microscopic animals play a far greater part than the larger ones.

It is well known that the Globigerina ooze covering the bottom of the Atlantic ocean, and other similar deposits, are largely composed of the remains of minute animals. Also the plankton, the floating fauna, composed mainly of animals without calcareous or siliceous organs, contributes very largely to the formation of bitumen.

Of great interest are the observations made by Andrussow and Lang in the Black and Caspian seas. The Adschidarja, a bay having an area of 15,500 sq. km., that is, as large as Saxony, is connected with the Caspian by a channel 100 to 500 meters wide. Owing to a difference in level, there is always a current flowing at the rate of 64 meters a minute into this bay. The water in the bay has the density 17° Bé., while that of the sea is 0°.5 to 1° Bé., so that all animals carried in by the current are killed and their bodies are deposited in great beds. Great numbers of fish also pass through the canal during the spawning season and die when they reach

the bay. These animal remains are more or less mingled with sand and dust carried into the bay by violent winds from the surrounding steppes. In time the bay will be completely filled in. The occurrence of fish remains, in connection with bitumen and petroleum deposits, is an important indication.

It was noticed by the Russian deep-sea expedition that, in parts of the Black Sea where the water is undisturbed by currents, there is so much hydrogen sulphide in solution that no animals can live, and there are large deposits of animal remains slowly decaying. Andrussow believes that the Black Sea and the Mediterranean bear the same relation to one another, as the Caspian Sea and Adschidarja. In the Red Sea, also, we find a somewhat similar state of affairs combined with an overproduction of animal life. The masses of tarry substance, and the oily surface often seen there, go to prove the truth of this theory.

The deposits of petroleum at Baku and the surrounding regions are nearly all tertiary. During that period there was an immense sea which became shallower as the land rose, and the Aral and Caspian seas, and other bodies of water, were cut off. It is certain that the menilite slate in which the petroleum occurs is of marine origin. Szajnocha laid stress on the fish remains found in this slate. He estimated that if the annual deposition of fish equaled the production of the fisheries in the northern waters of Europe, and the oil from these yielded only 50 per cent of petroleum, a period of only 2,560 years would have sufficed to produce the entire Carpathian petroleum deposit. Such a period is but a geological day.

In one or two fossil beds there have been found ammonites and mussels, with the shells filled with petroleum.

Engler does not deny that diatoms and other plants may yield petroleum, but regards it as very improbable that the larger petroleum deposits were formed from diatoms. The invariable presence of salt and brine indicates marine origin, as does also the geological evidence. For that reason Stahl's theory is preferable to that of Kraemer and Spilker. Höfer showed that the petroleum deposits have no connection with beds of turf, lignite, or coal, which are of fresh water origin.

The decay of the diatoms would yield at most 0.05 to 0.1 per cent of ammonium carbonate, so that it is very unlikely that their siliceous coverings would be dissolved, as suggested by Kraemer and Spilker.

It is not safe to say that the bitumen of peat-bogs is derived from diatoms, for Guignet and Durin have shown that the

wax extracted from peat by solvents closely resembles that obtained from living moss and other plants.

Quite recently Kraemer and Spilker[1] have published a modification of their theory. By extracting various kinds of peat, turf, and pyropissite with hot benzene or toluene, they came to the conclusion that the amount of wax is independent of the number of diatoms found in the material extracted. It is their belief that many other kinds of algæ besides diatoms have contributed to the wax, as it has been shown that oil drops are contained in the cells of the *Ulothrichaceæ*, *Phyllosiphoniaceæ*, and the *Vaucheriaceæ*. In the course of thousands of years everything but the oil would decay. Animal fats very soon become rancid.

When distilled under atmospheric pressure the crude wax yielded the same products as when distilled under considerable pressure. With reduced pressures, however, a wax-like distillate was obtained, while an asphalt-like mass, containing coke and sulphur, remained in the retort. The wax, when redistilled, came over unchanged. When first heated under reduced pressure, the crude wax yielded carbon monoxide and dioxide, hydrogen sulphide, and water with an acid reaction. If further heated under atmospheric pressure, methane, olefines, and carbon dioxide escape, while a semi-liquid mass of petroleum hydrocarbons passes over. The water smells of acetic acid and its volatile homologues. It is, therefore, probable that the crude wax contains easily decomposed substances, besides a mixture of a monacid ester mixed with free acid. This was shown by determining the acid number and saponification number of different specimens of wax. By saponification an acid approximating arachidic, behenic, and lignoceric acids in composition and melting-point was obtained. It was probably a mixture of all three acids, possibly with higher homologues. The alcohol set free contained 20 to 22 carbon atoms, and was probably a mixture also. No traces of glycerides were found.

These esters would easily yield methane, carbon dioxide, paraffins, and olefines when distilled under pressure. Naphthenes would be produced by ring formation. Hence the differences noted in various kinds of petroleum are not to be explained by differences in the raw materials, but are caused by dynamic agencies,—pressure and heat.

The presence of sulphur, and of organic sulphides formed from it, is due to sulphur bacteria.

Mineral wax is an important product intermediate between algal wax and petroleum. They were able to show that it

[1] Ber. d. chem. Ges., 35, 1212 (1902).

contains small quantities of an ester. It also contains sulphur and resin, and yields water, volatile fatty acids, and carbon dioxide when distilled, all of which shows its relationship to algal wax. The ash of mineral wax was shown to be similar in composition to that of a recent diatomaceous deposit.

Animal remains may have occasionally formed some petroleum, but the presence of sulphur and the rare occurrence of nitrogen compounds stand in the way of Engler's theory. Calculations are given to prove the possibility of the formation of the vast deposits of wax and oil from algæ.

It seems to the reviewer that very little has been added by the last paper. As pointed out by Engler, it is not improbable that petroleum may be of both animal and vegetable origin, and it is for the geologist to decide in any given case.

C. E. WATERS.

OBITUARY.

The *Berichte* of May 10th contains a brief notice of the death of Professor von Pechmann, of Tübingen, on April 19th. In October last an illness so affected his mind that he was compelled to spend the winter in a sanatorium for nervous diseases. He seemingly recovered, and at the beginning of this summer-semester returned to his work, but broke down again, and in an acute attack of melancholia, swallowed prussic acid.

Freiherr Hans von Pechmann was of a distinguished Munich family. He was a pupil of von Baeyer, at Munich, where he took the Ph.D. degree, and became Privatdocent. In 1884 he was given the chair of analytical chemistry, in Munich, made vacant by the death of Clemens Zimmermann. In 1895 he accepted a call to the full professorship in Tübingen.

Von Pechmann was of a very genial disposition, a delightful companion and friend, and an indefatigable worker in the field of organic chemistry. His fellow-student and friend, Professor Königs, of Munich, is to write an article on his investigations for the *Berichte*.

E. R.